VOLUMINA JURASSICA, 2024, XXII: 35–58
DOI: 10.7306/VJ.22.4

Principles of calcite macrofossil sampling and analysis for geochemical studies on Mesozoic palaeoenvironments

Clemens V. ULLMANN[1]

Keywords: macrofossils, diagenesis, sampling, palaeoenvironment, biomineralisation, geochemistry.

Abstract. Macrofossil carbonate is extensively used for palaeoenvironmental and chemostratigraphic research, especially for the reconstruction of Mesozoic and Paleozoic environments, climates and Earth system evolution. Work on such materials has allowed to chart geochemical signatures of biomineralisation and diagenetic overprints. This information, in conjunction with studies on modern analogues, allows placement of newly obtained results into a well-established conceptual framework of geochemical and structural overprints on macrofossils.

The reliability of geochemical research using Mesozoic macrofossils can be optimized by taking into account these general patterns of fossil diagenesis and tendency for exhibiting metabolic effects that bias palaeoenvironmental proxy incorporation into biominerals. Such biases are specific to individual taxa and successions and have to be tested in each study to provide quantitative constraints on preservation. Due to the large potential range of the expression of post-depositional alteration, analysis of relevant diagenetic phases and altered fossil materials should always complement study of the best-preserved material.

This contribution outlines principles behind this screening approach and provides guidance on general sampling and sample evaluation strategies. These strategies improve the confidence in the validity of analytical data from macrofossil carbonate for palaeoenvironmental interpretation, including for novel and easily altered geochemical proxies.

INTRODUCTION

Much of the pioneering work on palaeoenvironmental reconstruction using bio-minerals has been done on macrofossils. Building on the theory that oxygen isotope ratios in ancient carbonates could be used as a palaeothermometer, and that these ratios could feasibly be determined at sufficient precision for meaningful temperature estimates (Urey, 1947), analytical data from modern marine invertebrates and Mesozoic macrofossils (oyster and belemnite calcite) were soon published (Urey, 1948). Shortly after this, the calcite of rostra of the belemnite species *Belemnitella americana* from the Maastrichtian PeeDee Formation of South Carolina became the source of the reference gas at the Institute of Nuclear Studies in Chicago (PDB, Urey *et al.*, 1951). Since then, the importance of macrofossils has been manifest through *B. americana* as the "PeeDee Belemnite", serving as the global isotopic standard for biogenic carbonate C and O isotope analysis which still stands as the isotopic anchor for biological carbonates (Stichler, 1995).

Palaeoenvironmental reconstructions of the Paleozoic and Mesozoic were built, beginning with few data points (Urey *et al.*, 1951), but increasing in detail (*e.g.*, Bowen, 1960; Compston, 1960; Bowen, Fritz, 1963), over time leading to large, macro-fossil calcite-based compilations (Veizer *et al.*, 1999; Dera *et al.*, 2011; Bodin *et al.*, 2015; Korte *et al.*, 2015; Hesselbo *et al.*, 2020). The attention of geochemists soon broadened to microfossils (*e.g.*, Emiliani,

---

[1] University of Exeter, Department of Earth and Environmental Sciences, Penryn Campus, Treliever Road, Penryn TR11 9FE, United Kingdom; c.ullmann@exeter.ac.uk.

1954, 1955) which are now generally the preferred substrates for studying the Cenozoic and partly also late Mesozoic (*e.g.*, Zachos *et al.*, 2001; Westerhold *et al.*, 2020), with different sampling and sample treatment approaches established for such materials (*e.g.*, Martin, Lea, 2002; Vetter *et al.*, 2013). However, macrofossils are still the most important biological substrates to reconstruct Mesozoic and Paleozoic environments. Where records with sub-annual resolution are essential, they are also used for the more recent geologic past (*e.g.*, Jones, Allmon, 1995; Schöne *et al.*, 2004) and they lend themselves to analysis of isotopic systems that tend to require comparatively large sample sizes. Utilising latest technological advances and scientific understanding of biomineralisation as part of the sampling strategy will thus continue to positively impact macrofossil research and palaeoenvironmental research in general.

Complications that limit the direct applicability of measured oxygen isotope ratios of fossil carbonate have been apparent since the first attempts to use this proxy, and these considerations are still relevant today. The existence of a vital effect, biasing isotopic ratios away from isotopic equilibrium with the liquid in which the carbonate is secreted, was mentioned as a distinct possibility beginning with the first publications on biogenic carbonate (Urey, 1948; Urey *et al.*, 1951). Such effects were substantiated for various organisms (McConnaughey, 1989; Wefer, Berger, 1991; Carpenter, Lohmann, 1995; Sørensen *et al.*, 2015), with research continuing to uncover increasingly subtle offsets and effects specific to types of biomineral subunits and/or sample position within a hard part (*e.g.*, Takayanagi *et al.*, 2015; Ullmann *et al.*, 2015; Hoffmann *et al.*, 2016; Immenhauser *et al.*, 2016). Equally, the risk that carbonates could undergo isotopic exchange after deposition as a consequence of metamorphic reactions, recrystallisation, diffusion, closed and open system diagenesis was discussed on a theoretical level very early on (Urey, 1948; Urey *et al.*, 1951). Building on these first accounts, observations from fossil material highlighted the existence of diagenetic trends that could be traced with geochemical indices (Lowenstam, 1961; Curtis, Krinsley, 1965; Longinelli, 1969; Veizer, 1974, 1983; Brand, Veizer, 1980; Al-Aasm, Veizer, 1982, 1986a, b; Marshall, 1992; Ullmann *et al.*, 2013a; Fernandez *et al.*, 2021). Such empirical work on fossil examples was also supplemented by experimental studies (*e.g.*, Riechelmann *et al.*, 2016; Guo *et al.*, 2019), and theoretical work (*e.g.*, Banner, Hanson, 1990; Fantle *et al.*, 2010) that, taken together, have yielded a solid understanding of the expression and expected magnitudes of post-depositional alteration (Swart, 2015; Ullmann, Korte, 2015). Nevertheless, the issues of the expression of diagenesis and the confident identification of diagenesis-induced biases on proxy records remain amongst the biggest obstacles to palaeoenvironmental research. This is particularly the case for research on marine records going beyond the Jurassic, where target sedimentary successions have (nearly) invariably been subject to a degree of tectonic displacement. This is of importance, because such tectonic episodes have the potential to cause complex diagenetic reactions that occur when sediments and their fossil contents re-equilibrate with changing pressure, temperature and chemical conditions. Research on diagenesis is still ongoing also because new proxies are starting to be utilised that are highly sensitive to contamination, such as isotope ratios of lithium and boron whose concentrations in fossil carbonates are typically much lower than in the enclosing sedimentary matrix (*e.g.*, Paris *et al.*, 2010; Washington *et al.*, 2020; Li *et al.*, 2021). Equally, subtle recrystallisation or diffusion which are relevant for clumped isotope thermometry (*e.g.*, Henkes *et al.*, 2014; Fernandez *et al.*, 2021) may not be picked up by conventional screening.

The purpose of the present contribution is to illustrate existing practices of sampling and assessing Mesozoic carbonate (with an emphasis on low-Mg calcite) macrofossils for palaeoenvironmental research. Benefits and shortcomings of various approaches to sampling and determination of fossil preservation are highlighted, and guidance for suitable sampling is provided. This guidance is in principle also applicable to the study of fossils from other time periods, but the focus here is on fossils and palaeoenvironmental settings that are typical of Mesozoic strata. A set of general guiding principles for preparation of such materials are provided that can be used to improve the reliability and scientific impact of generated data. Finally, an attempt is made to generalize criteria for the assessment of macrofossil-based work. These criteria may be taken to judge what the most important limitations of case studies are that may need to be mitigated.

SAMPLING STRATEGIES TO CONTROL DIAGENESIS

A fact of far-reaching importance is that no fossil found in the geological record is compositionally exactly the same as at the point that the animal died. Even though the term ‘pristine’ is sometimes used in the literature to describe very well-preserved fossil shell materials (*e.g.*, Jenkyns *et al.*, 2002; Brand *et al.*, 2010; Korte *et al.*, 2015), this terminology should probably be avoided and replaced by more realistic descriptors. As diagenesis causes structural and geochemical modifications of target fossil materials, when taken for palaeoenvironmental work, samples affected by alteration beyond acceptable limits need to be identified and excluded from further consideration. Thus, screening for post-depositional overprints stands at the beginning of the evaluation of macrofossil material, and sampling of fossil remains needs to be carried out so that this screening is as effective as possible. The inextricable link between understanding fossil geochemistry and fossil diagenesis warrants examination how sampling procedures can be optimized to apply all relevant techniques for studying diagenesis.

Studies of the general effects of post-depositional alteration of shell materials have been conducted, and a number of well-known references relating to previous research are often quoted (*e.g.*, Brand, Veizer, 1980, 1981; Veizer, 1983; Al-Aasm, Veizer 1986a, b; Marshall, 1992). While this work was pioneering at the time, it established a consensus approach to assessing (macro)fossil preservation that was partially driven by the analytical limitations of the time, particularly in relation to the rate at which samples could feasibly be analysed. With much more rapid and precise analytical methods now routinely available to obtain information about the isotopic composition (*e.g.*, Spötl, Vennemann, 2003; Pin *et al.*, 2014) and element concentrations (*e.g.*, Rosenthal *et al.*, 1999; Schrag, 1999) in geomaterials, it is possible to build on the general understanding of expected diagenetic trends and to determine their specific manifestation in studied localities with comparative ease. To this end, stratigraphically resolved diagenetic endmembers and alteration trends within fossils, sometimes down to the genus level, may have to be determined (*e.g.*, Brand *et al.*, 2010; Harlou *et al.*, 2016). This calls for a specific sampling approach, including analysis of bulk sediment, diagenetic end-members, and (partially) altered fossil material, as explained in more detail below.

GENERALIZED ASSUMPTIONS FOR GEOCHEMICAL TRENDS OF ALTERATION

In most diagenetic environments, diagenetic processes that modify the geochemistry of fossil shells follow qualitatively the same trends, namely a loss of Sr, Na, ^{18}O, ^{13}C and gain of Mn, Fe, ^{16}O and ^{12}C (*e.g.*, Brand, Veizer, 1981). These geochemical trends are typical of diagenetic stabilization during interaction with meteoric waters (*e.g.*, Brand, Veizer, 1981), a scenario that very often applies. However, a wider variety of trends was equally highlighted, for instance for carbon and oxygen isotopes responding to marine cementation or burial diagenesis (Al-Aasm, Veizer, 1986a, b). A summary of the wide array of possible diagenetic effects on bulk carbonate geochemistry has been given by Swart (2015), while more macrofossil-focussed descriptions were provided by Ullmann and Korte (2015). The available literature altogether highlights that diagenesis is a ubiquitous phenomenon even in apparently well-preserved materials and that there is no standard alteration pathway for geochemical proxies in biological carbonates. Some common assumptions can be made about fossil preservation, which often tend to hold in qualitative terms but need to be defined carefully in relation to the local context to be useful to effectively discriminate well-preserved from poorly-preserved material.

Comparison of fossil chemical composition to modern analogues

Modern biological carbonate is compositionally distinct from abiogenic carbonate (*e.g.*, Carpenter, Lohmann, 1992; Ullmann *et al.*, 2018). Therefore, a good argument about preservation can potentially be made where the chemical fingerprint of a fossil matches that of modern analogues rather than that of inorganically precipitated carbonate. By the 1950s (*e.g.*, Odum, 1951; Chave, 1954), the utility of element concentrations in biological carbonate to reconstruct temperature and ocean chemistry was considered, and the Mg and Sr content of biological carbonate was soon after charted in considerable detail (Dodd, 1967). Compilations of geochemical compositions of relevant groups based on large numbers of individual quantitative analyses and dozens of taxa now exist, e.g. for brachiopods (Brand *et al.*, 2003, 2013) and barnacles (Ullmann *et al.*, 2018). Because the distinct geochemical fingerprints of these organisms are expected to be erased by diagenesis, comparison to the geochemical composition of modern taxa has been abundantly used to argue for the preservation of fossil representatives (*e.g.*, Popp *et al.*, 1986; Veizer *et al.*, 1999; Mii *et al.*, 2013).

While comparison of key element concentrations between modern and fossil taxa can be quite successful, utilizing the entire observed compositional range of modern analogues is not typically an optimal strategy. In diverse groups of animals there are commonly chemical distinctions relating to finer taxonomic subdivisions, as for instance seen in the progressively increasing Sr and Mg content from rhynchonellid and terebratulid brachiopods through thecideid brachiopods to the high Mg calcite of craniid brachiopods (Brand *et al.*, 2003; Ullmann *et al.*, 2017a; Fig. 1).

Equally, in modern barnacles the majority of taxa has been found to secrete low Mg calcite, while the species *Capitulum mitella* is distinct in secreting alternating bands of low and high Mg calcite (Ullmann *et al.*, 2018). Even where a wide range of taxa have been analysed in modern environments, these analyses may not be entirely representative of the fossil populations (Fig. 1). For instance, modern brachiopod analyses have covered terebratellinids comparatively well, while only few rhynchonellid taxa have been published on in detail. Studies on fossil material on the other hand preferentially use rhynchonellids due to the absence of punctae (Perez-Huerta *et al.*, 2009) and the lack of pronounced vital effects in the secondary shell layers of the lat-

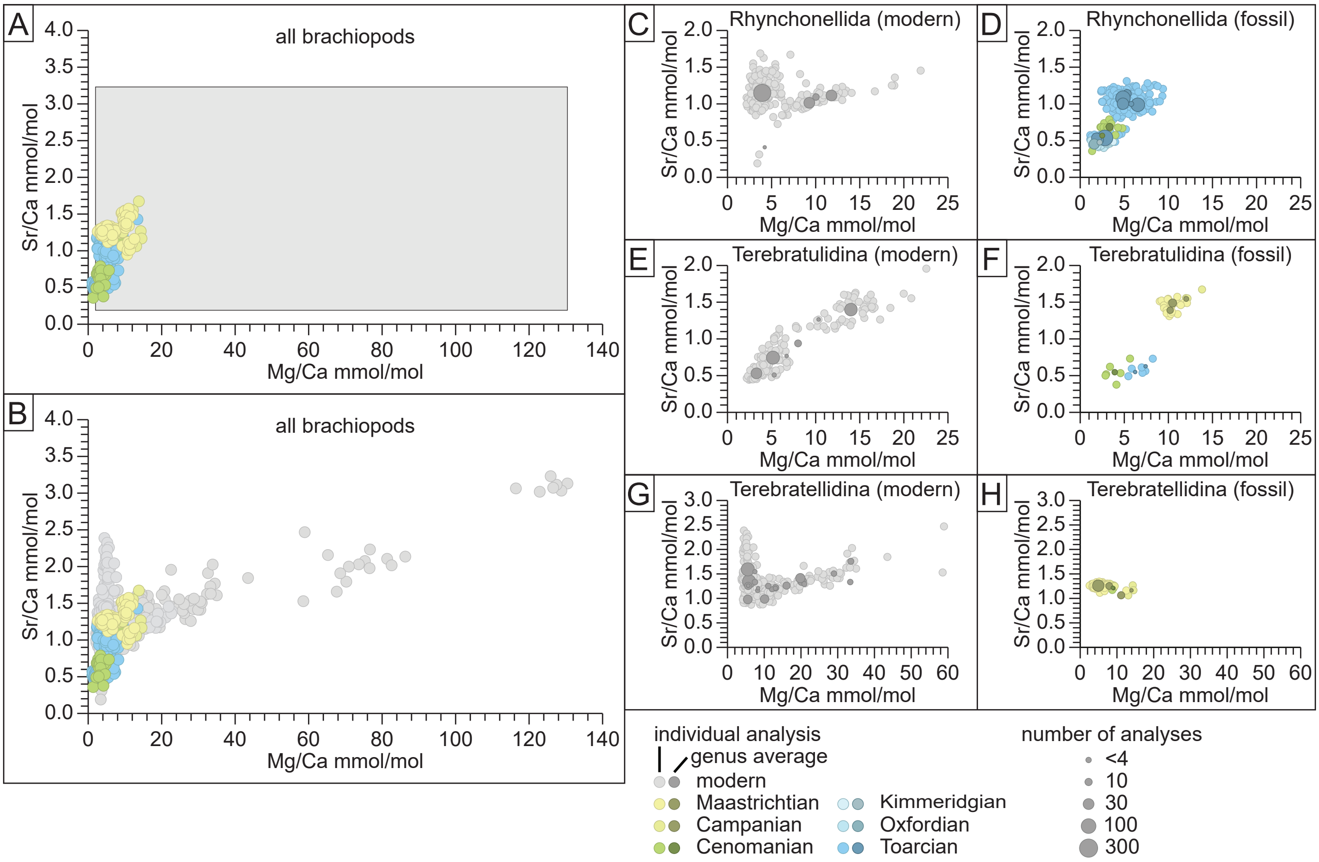

Fig. 1. Range of Sr/Ca and Mg/Ca ratios in modern and fossil brachiopods

A. Grey box showing full range of either proxy without co-variation in modern taxa; **B.** Individual analyses for modern and fossil taxa, highlighting also the co-variation of both element/Ca ratios in brachiopods. **C–H.** finer differences between brachiopod orders/suborders, illustrating also the imbalance in taxonomic breadth between modern and fossil taxa that have been reported on.

C, E, G. Modern data compiled from Brand *et al.* (2003) and Ullmann *et al.* (2017a, b). D, F, H. Fossil data from Voigt *et al.* (2003), Jelby *et al.* (2014), Wierzbowski (2015), Harlou *et al.* (2016) and Ullmann *et al.* (2020)

ter (*e.g.*, Parkinson *et al.*, 2005; Ullmann *et al.*, 2017a). Nevertheless, if comparison is made to the compositional range of modern taxa, a selective approach regarding the comparator taxa is typically required to allow for meaningful assessments of the true expected natural range of geochemical data.

Besides taxonomic differences, the concentration of a number of elements in biological calcite is driven by environmental factors rather than species-specific incorporation. For instance, Mn and Fe tend to relate to the ambient bioavailable levels of these elements (Freitas *et al.*, 2006; Barbin *et al.*, 2008), e.g. at human-made structures (Ullmann *et al.*, 2018) and river outlets (Almeida *et al.*, 1998), even though a direct link can be hard to establish (Cravo *et al.*, 2007; Freitas *et al.*, 2016). Linking the reported concentration of such elements with the taxon for which it was reported would therefore be problematic. Instead, modern analogue comparisons are likely to be more successful if focusing on elements which are uniformly distributed in seawater and whose concentration in biological shell materials is therefore determined largely by the (species-specific) distribution coefficient between water and carbonate. Even for these elements obstacles exist, namely the secular changes in ocean chemistry which conceivably complicate direct comparison between fossils and modern taxa (Odum, 1951; Stanley, Hardie, 1998; Steuber, Veizer, 2002; Ullmann *et al.*, 2013b; Fig. 1). Indeed, the Mesozoic brachiopods illustrated in Figure 1 tend to exhibit somewhat lower Mg/Ca ratios than comparable modern taxa. This might be related to a higher Mg/Ca ratio of modern seawater compared to estimates for the Mesozoic (*e.g.*, Stanley, Hardie, 1998; Coggon *et al.*, 2010). However, sampling bias cannot be excluded as an explanation due to the small number of well-described modern and fossil taxa that can be relied upon for granular comparison.

Overall, comparison of fossil chemistry to the chemical composition of modern taxa is currently held back by the still limited size of compilations for geochemical fingerprints of modern and well-preserved fossil species. In the future, however, matching chemical signals with closely related species will be very valuable to ascertain good shell preservation. Obtaining basic element data for taxonomically identified fossil taxa should increasingly become the norm, in time permitting more robust matching of compositional ranges as means of assessing preservation, ideally against information on closely related taxa from the same time and ideally same region and depositional environment.

Mn/Sr ratios and global Mn, Sr, or Fe limits

A variation on the theme of matching fossil data to the compositional range of modern taxa is to impose limiting concentrations of various elements or sometimes ratios of elements as a marker for preservation. Qualitatively, a reduction of Sr and a gain of Mn and Fe in diagenetic environments is likely (Brand, Veizer, 1980; Carpenter, Lohmann, 1992) and these elements are often used to set quantitative preservation markers (see Ullmann, Korte, 2015 for a list of examples). As modern biogenic carbonates typically show an enrichment in Sr over abiogenic carbonates (Dodd, 1967; Carpenter, Lohmann, 1992) and comparatively low Mn and Fe concentrations (*e.g.*, Brand *et al.*, 2003; Ullmann *et al.*, 2018), such an approach is qualitatively justified. However, there are wide compositional differences in diagenetic endmembers (see Ullmann, Korte, 2015 for some examples), as well as primary biogenic carbonates, that require attention. Figure 2 illustrates the pitfalls in generalizations and highlights the necessity of a more refined approach, including the routine sampling and determination of diagenetic endmembers.

In the case of Jurassic (Toarcian) fossils from Spain (Fig. 2A–C), it is clear that different fossil types occupy distinct areas in geochemical cross plots, and therefore assigning Sr and Mg limits for good preservation would only be useful if refined for these distinct groups. In this example, geochemically distinct samples falling outside the typical range in these fossils generally show elevated Mg, Mn (and Fe, not shown) levels, and the Mg trend in bivalves hints at a diagenetic end-member similar to bulk rock rather than calcite cement (Fig. 2A). However, besides belemnite samples, the Sr content of the fossil shell fragments analysed for this study is not very different from that observed in bulk rock. Consequently, alteration-imposed changes in Sr appear to be smaller than the natural variability of Sr content in virtually all measured samples. Sr content – even if specifically set for different fossil groups – in this scenario would therefore not be a useful marker of preservation because it is not diagnostic for either state. Mn content is markedly higher than background in some samples, with bulk rock compositions still a viable model for the diagenetic endmember. Taken together, this allows justification of the use of limiting Mn (as well as Fe which is not shown here, and taxon-specific Mg) contents for the fossils, and to predict that biases on other geochemical proxies imposed by alteration may be modelled using the enclosing bulk rock as an endmember.

In the case of a Toarcian belemnite from the Cleveland Basin of the UK (Fig. 2D–F), a somewhat different picture emerges, where intra-specimen variability of Mg and Sr is too large to observe any meaningful correlation with the composition of local cements. Nevertheless, distinct enrichments in Mn that are associated with minor depletions in Sr, as expected for fossils that are secreted with a comparatively high primary Sr content, are seen. Here, it is largely the co-variation of C and O isotopes in Mn enriched samples that trend towards the isotopic ratios of the cement that justify the use of Mn content as a criterion for preservation.

In either of the example cases outlined above, limiting element concentrations could only be defined because samples were also measured of diagenetic phases, and these limits could then be set individually with the magnitude of bias imposed on target proxies in mind.

C and O co-variation

The degree of co-variation between C and O isotope ratios in ancient carbonates is often taken as one of the principal tests for retention of a primary signature, where a strong positive correlation between the two ratios indicates (partial) overprint (*e.g.*, Veizer *et al.*, 1997; Gröcke *et al.*, 2007; Alberti *et al.*, 2019). While this approach can highlight preservation issues, positive correlation of C and O isotope ratios may occur without a strong diagenetic component, and, importantly, diagenetic overprints may not lead to a positive correlation between these ratios. It is critical to consider the geological materials studied and the local diagenetic context to judge which of these scenarios may apply.

Partial diagenetic modification of carbonate toward an endmember depleted in ^{13}C and ^{18}O such as modelled e.g. by Banner and Hanson (1990), (for empirical examples of this see for instance Ullmann *et al.*, 2015; Godet *et al.*, 2016; Jenkyns, Macfarlane, 2022) is one of the main causes of a strong positive co-variation between C and O isotope ratios in ancient carbonates. However, the same effect is created by the analysis of materials that exhibit well-expressed vital effects seen in certain parts of biological carbonate, such as in corals (McConnaughey, 1989; Wefer, Berger, 1991) or brachiopods (Carpenter, Lohmann, 1995; Parkinson *et al.*, 2005; Ullmann *et al.*, 2017a). These biological archives naturally contain portions of carbonate that are highly enriched in ^{12}C and ^{16}O, while other parts are more

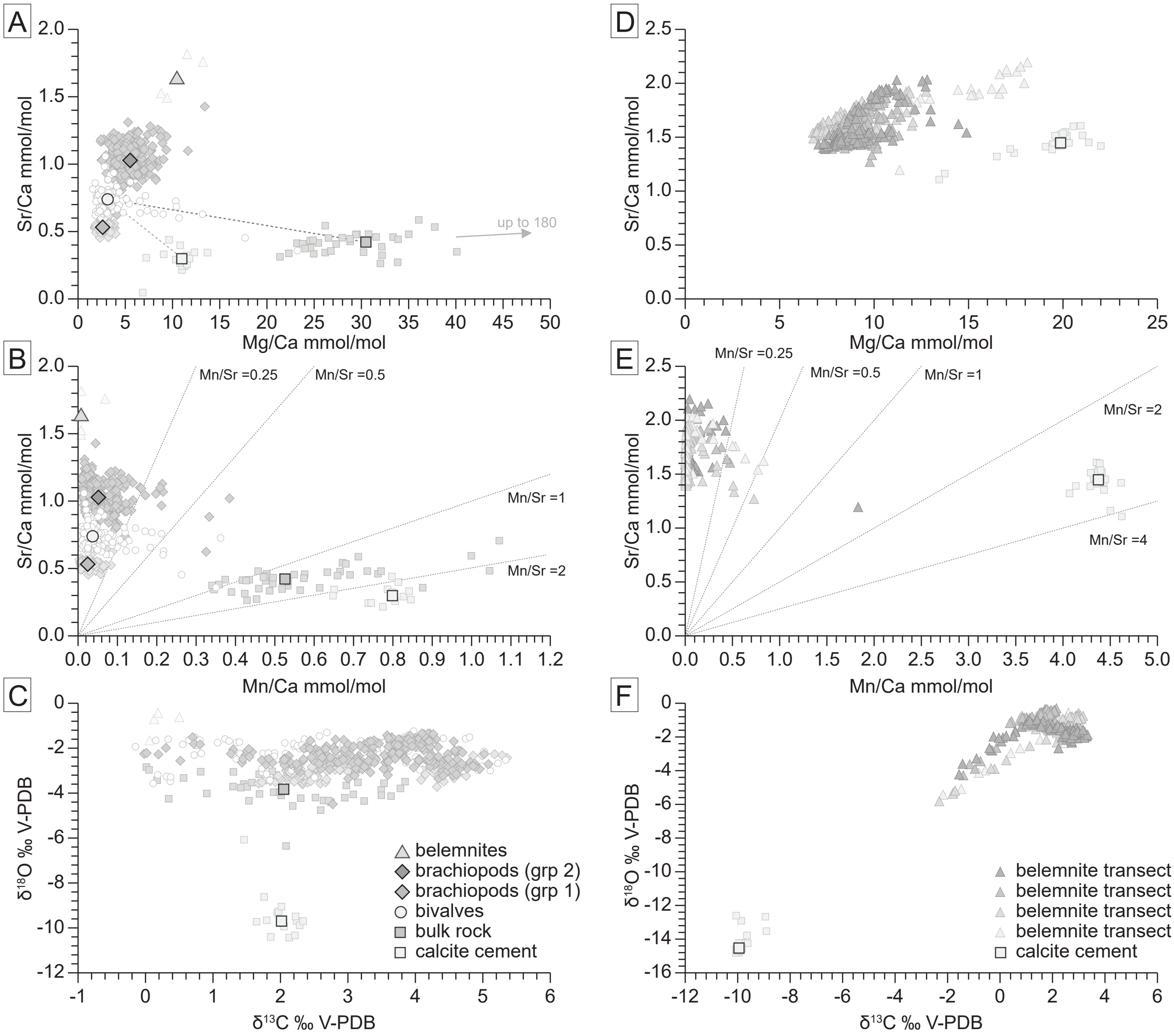

Fig. 2A–C. Range of element concentrations and isotopic ratios in macrofossils in Toarcian strata from Central Spain (data from Ullmann *et al.*, 2020). D–F. Range of element concentration and isotopic ratios in multiple transects through one Toarcian belemnite rostrum of the species *Passaloteuthis bisulcata* from the Cleveland Basin, Yorkshire, UK (data from Ullmann *et al.*, 2015)

Also shown as dotted lines in the top panel are mixing lines of fossil endmembers with either bulk rock or cement in the top left and selected Mn/Sr ratios in the middle panel. Small symbols relate to individual measurements while larger symbols with stronger outline show median for each sample type

closely matched with expected ratios of carbonate secreted in isotopic equilibrium with ambient liquids. Equally, sedimentary successions covering longer periods of geologic history, where climatic and environmental change caused parallel shifts in palaeotemperature/salinity and carbon cycle may yield such covariation (*e.g.*, Brand *et al.*, 2012). For instance, during some of the prominent Mesozoic phases of deoxygenation in marine environments that are typically linked with (substantial) warming and coincident carbon cycle perturbation (Jenkyns, 2010; Suan *et al.*, 2010; Bodin *et al.*, 2015), such co-variation would naturally be imposed on the carbonate record.

On the other hand, there are multiple reasons why diagenetic co-variation of oxygen and carbon isotopes is not strongly developed. For co-variation to be observed, a studied series of samples needs to exhibit a heterogeneous degree of preservation and two distinct compositional endmembers, the primary and diagenetic endmember. If preservation is largely skewed to one or the other, only some outliers from a general compositional field would be seen. If there are multiple diagenetic endmembers, no linear covariation of proxies can be postulated, and if the diagenetic endmember lies within the natural variability of the samples (Harlou *et al.*, 2016) or only has a distinct composition for either C or O isotope ratios (Ullmann *et al.*, 2020), no co-variation would be imposed by partial overprint either. Even if the diagenetic endmember is well-defined and compositionally distinct, to cause a strong co-variation of isotopic ratios it has to be distinct enough to cause data variance that exceeds the primary natural variability. Depending on the diagenetic environment, types of studied fossils, and geologic time interval, this may well not be the case.

The two case studies shown in Figure 2 illustrate some of these points. In fossils from Spain covering the Early Jurassic Toarcian Oceanic Anoxic Event (Ullmann *et al.*, 2020; Fig. 2A–C), large-scale changes in carbon isotope ratios as well as oxygen isotope ratios in fossils are seen as a consequence of changing environmental conditions. The local diagenetic endmember (akin to bulk rock composition) is isotopically indistinct with only marginally ^{18}O depleted oxygen isotope signature, so even moderate alteration of fossils would not be visible easily in a cross plot of carbon versus oxygen isotope ratios in this case. Even if the samples were compromised by addition of isotopically more extreme diagenetic cements, as a few measurements indicate, these would only be expected to yield a marked shift in δ^{18}O. Since δ^{13}C in this case would change only slightly, no strong co-variation of these two isotopic systems would be seen even when including moderately to poorly preserved material with a strong cement presence.

Contrasting this, individual transects through a belemnite rostrum from the Cleveland Basin, UK (Fig. 2D–F), show clear and very strong linear co-variation of C and O isotope ratios grading towards the isotopic ratios seen in local calcite cement. Therefore, the co-variation of the isotope ratios is clearly linked with heterogeneous sample preservation in this case. Even in this relatively clear-cut case, though, the fossil endmember is different in each transect due to the comparatively high intra-specimen variability of the isotopic ratios and different interval of the ontogenetic sequence that was partially overprinted in each of these transects.

Altogether it is risky to presume that a correlation between C and O isotope ratios will occur in overprinted material and can thus be used as a quality control marker. Instead, obtaining the same suite of proxies for diagenetic phases as for target fossil materials provides the most robust possible constraints on the degree of preservation (or diagenetic overprint), because magnitude of change and the proxy that shows compromised shell material best will depend on the local setting. Indeed, these overprints may be taxon- and time-dependent, potentially requiring quite granular analysis in certain settings (Brand *et al.*, 2012; Harlou *et al.*, 2016).

SHELL STRUCTURE ANALYSIS

While crystallographically identifiable as calcite, aragonite, or other carbonate polymorph (despite distinct crystal lattice distortions, Pokroy *et al.*, 2006; Zolotoyabko *et al.*, 2010), the morphologies of macro-invertebrate carbonate are highly distinct at the macroscopic level and at the scale of individual crystal units (shell fibres) (Checa *et al.*, 2007; Ullmann *et al.*, 2015; Cusack, 2016; Checa, 2018; Ye *et al.*, 2018). These distinct shapes are thermodynamically unfavourable (Busenberg, Plummer, 1989), causing recrystallization to have a clear effect on shell fibre morphology and crystallographic parameters (*e.g.*, Brand *et al.*, 2007; Ullmann, Korte, 2015; Casella *et al.*, 2018). The study of the morphology of these individual crystals via optical or electron beam techniques is thus very useful to obtain qualitative information on dissolution, secondary precipitates, or (partial) recrystallization that fossil shell material suffered.

Because of the typically heterogeneous preservation of fossil shell materials, such analysis is best used in conjunction with other tools to study preservation, but it provides a useful additional dimension to the nature of diagenetic processes that shell material may have been exposed to, especially when unusual geochemical signatures are observed. It is therefore beneficial to prepare fossil specimens or fragments of their shells for dedicated optical or microscropic screening.

Optical assessment techniques test similar attributes, meaning that are multiple tools available to study the structural preservation of fossil hard parts. An initial optical assessment using a hand lens or binocular microscope can already be very informative for screening preservation, as recrystallisation for instance typically causes belemnite rostra to lose their transparency (Ullmann *et al.*, 2014; Ullmann, Korte, 2015) and brachiopods to lose the silky reflection on their secondary shell layers.

More advanced optical techniques such as studying polished sections using a petrographic microscope or via electron backscatter diffraction (EBSD) gives spatially resolved information about the structural integrity of individual subunits of the shell (*e.g.*, Ullmann *et al.*, 2014; Casella *et al.*, 2018). Individual fragments of shell can also be tested using scanning electron microscopy via secondary electron images, giving highly resolved imagery for the surface features of part of the shell, which allows to test for dissolution, recrystallisation and other secondary features imposed on the material (*e.g.*, Veizer *et al.*, 1999; Brand *et al.*, 2007; Korte, Hesselbo, 2011).

These insights, in conjunction with geochemical data, can be very powerful to reconstruct alteration process magnitude, timing, and type.

SAMPLE SELECTION AND CHEMICAL PRE-PROCESSING TO COMBAT OVERPRINTS

It has been shown for different invertebrate groups that there are geochemically distinct parts of their shell either in terms of element signatures (Ullmann *et al.*, 2015 for belemnites, Ullmann *et al.*, 2017a for brachiopods) or isotopic signatures (*e.g.*, Parkinson *et al.*, 2005). Equally, partial overprints of macrofossil calcite are usually spatially heterogeneous, which can be visualized by imaging and geochemical mapping techniques such as cathodoluminescence (*e.g.*, Savard *et al.*, 1995; Barbin, 2000, 2013; England *et al.*, 2006), µXRF (de Winter, Claeys, 2017), or PIXE (Bruckschen *et al.*, 1995; Veizer *et al.*, 1999).

Maintaining spatial integrity of fossil specimens before sampling takes place and noting the location from which samples derive is therefore critical for minimizing the possibility of inducing added variability and possible bias to proxy datasets. This means that pre-crushing of fossils before picking the best-preserved looking fragments is problematic and should only be done if there is no other viable means of exposing well-preserved fossil carbonate. A more suitable way of accessing well-preserved fossil material is to physically remove sediment and altered material, for example using a handheld drill, preparation needle, or scalpel, before extracting target material from such pre-cleaned surfaces.

For microfossils, chemical cleaning protocols to remove oxide crusts, etc., are commonplace. These procedures have been used also for macrofossils (*e.g.*, McArthur *et al.*, 2004; Harlou *et al.*, 2016), but should be employed carefully where they are necessary. Chemical pre-treatment of samples has the potential to bias geochemical results where hard parts are composed of different shell structures with somewhat differing resistance to acid attack. At the same time, acid pre-leaching of carbonate fossils is more likely to digest primary fossil material than altered parts because the recrystallized shell material approaches a thermodynamically more favourable form than the biogenic original (Busenberg, Plummer, 1989).

MULTI-LEVEL ASSESSMENT OF DIAGENESIS

A wide, and ever growing, range of geochemical proxies can be used for intricate reconstructions of palaeoenvironmental conditions and palaeoecology. Commonly, the potential for alteration of the more advanced proxies is similar or greater than for proxies that are routinely measured for macrofossils. Trace element proxies such as Li and B for instance are more susceptible to significant bias due to potential mobility in the crystal lattice, and the typically much higher Li and B levels in encasing sediments compared to the fossil materials (*e.g.*, Paris *et al.*, 2010; Pogge von Strandmann *et al.*, 2013); radiogenic isotope ratios such as $^{87}Sr/^{86}Sr$ may already be significantly biased by only small-scale diagenetic overprints (*e.g.*, Brand, 1991); clumped isotope ratios may respond to prolonged exposure to moderate-high temperatures without any traditional diagenesis marker picking this up (Fernandez *et al.*, 2021).

This places an extra burden of proof of preservation on any such more advanced proxy, where studied materials not only have to pass the usual scrutiny, but also the additional tests put in place to ascertain sufficient preservation for the specific proxy. At the same time, interpretation of such more advanced proxies is typically also assisted by a robust framework of well-established proxies which commonly arise from basic optical and chemical screening of fossils. It follows that fossil materials taken for palaeoenvironmental reconstructions should always be tested for structural and basic geochemical preservation in addition to testing the preservation of more advanced proxies. This approach, when applied rigorously, allows more faith to be placed on the validity of advanced proxies and also provides crucial metainformation contextualizing these data.

SAMPLE SIZE, SAMPLE TYPE AND POSITION

Macrofossils are typically characterized by growth rates that are high enough to allow for the extraction of palaeoclimate parameters at greater than annual resolution. This potential is utilized in the field of sclerochronology for proxy-driven climate studies of the recent past (Jones, 1983; Butler *et al.*, 2013; Schöne, 2013) and increasingly also for deep time applications (*e.g.*, Steuber, 1996; Mettam *et al.*, 2014; de Winter *et al.*, 2020; Huck, Heimhofer, 2021; Posenato *et al.*, 2022). While knowledge about the amplitude of seasonality and temporally highly resolved proxy data in general are important to constrain palaeoenvironments, more often macrofossils from the Mesozoic are used for chemostratigraphic purposes and to constrain temporal evolution of palaeotemperatures and other palaeoenvironmental parameters. In environments and periods of Earth history where seasonality was high, the high shell secretion rate thus usually causes variability in the data that has to be considered when attempting to establish representative chemostratigraphic trends.

SAMPLING STRATEGIES FOR COMMON MACROFOSSIL GROUPS

There is a wide range of macrofossils that can be studied to reconstruct Mesozoic palaeoenvironments, amongst which belemnites, brachiopods, and bivalves are probably the most favoured (*e.g.*, Bailey *et al.*, 2003; Dera *et al.*, 2011; Bodin *et al.*, 2015; Korte *et al.*, 2015; Ferreira *et al.*, 2019; Hesselbo *et al.*, 2020). Different sampling approaches are advised for each of these groups, and even within individual groups, ongoing research is revealing increasing detail about general biomineral properties as well as taxon-specific signals.

While general element concentration ranges and types of shell structures are known well for fossil materials, the finer details relating to taxon-specific shell structural and geochemical properties remain poorly covered. This paucity of taxon-specific data for fossils can in time be mitigated by clearly documented work on taxonomically identified material, for which detailed structural and geochemical properties are reported. However, some general recommendations in relation to sampling these groups can already be given.

For belemnite rostra, the most coherent geochemical information can be derived from the intermediate growth increments of its stem region, where isotope and element/Ca ratios appear to be least affected by effects of shell secretion rate and biomineral shape (Ullmann *et al.*, 2015; Ullmann, Pogge von Strandmann, 2017). Even in this area, though, complications are expected from the intergrowth of two distinct calcite varieties (Hoffmann *et al.*, 2016), which can only be separately determined using high spatial resolution instrumentation such as laser ablation, electron probe microanalysis, or secondary ion mass spectrometry (Hoffmann *et al.*, 2021). The implications and degree of possible bias on palaeoenvironmental reconstructions from the indiscriminate analysis of bulk rostrum calcite are yet to be fully understood. Complications equally pertain to the unsettled debate about belemnite ecology and life span (*e.g.*, Naef, 1922; Urey *et al.*, 1951; Price, Sellwood, 1997; Podlaha *et al.*, 1998; Rexfort, Mutterlose, 2009; Wierzbowski, 2013; Ullmann *et al.*, 2014; Hoffmann, Stevens, 2020), which can reasonably be assumed to be different for at least some belemnite taxa. Vital effects are clearly present in carbon isotope ratios of a subset of taxa (Sørensen *et al.*, 2015), even though there are instances where C isotope data are quite compatible with other fossil groups (*e.g.*, Korte, Hesselbo, 2011), making taxonomic work on fossils important and highlighting a need to look into these effects on a case-by-case basis. Studies focused on oxygen isotope ratios have considered vital effects as well, but here, potential offsets are more equivocal (Price, Passey, 2013; Vickers *et al.*, 2020; Wierzbowski, 2021), especially considering a potential cold bias in $\delta^{18}O$ (*e.g.*, Bajnaj *et al.*, 2020; Hoffmann *et al.*, 2021) requiring further detailed work. The above points highlight the importance of reporting taxonomic information, or – where unavailable – morphological detail and sampling position for belemnite samples.

Brachiopod data, considering their largely benthic habitat (Carlson, 2016), tend to be comparatively straightforward to interpret. For brachiopods, a general preference is to sample (where present) the secondary fibrous shell layers, ideally in the middle part of the valve, towards but not at the internal margin of the shell (*e.g.*, Romanin *et al.*, 2018). Here, vital effects appear to be least prominently expressed even in otherwise problematic groups such as terebratulids as established by detailed research on extant species (*e.g.*, Auclair *et al.*, 2003; Rollion Bard *et al.*, 2016). Nevertheless, minor but significant offsets in isotopic signatures compared to oyster fossils (for example) have been noted even in nominally ideal targets (Ullmann *et al.*, 2020), the reasons for which have not yet been investigated in detail. Brachiopods without punctae, e.g. rhynchonellids, are preferred for sampling, because punctae are often cemented with diagenetic carbonate, and may act as conduits for diagenetic fluids compromising fossil preservation (*e.g.*, Veizer *et al.*, 1999; Angiolini *et al.*, 2007; Fujioka *et al.*, 2019). Comparatively little is known whether the expression of geochemical data may be specific to the studied valve (but see Ullmann *et al.*, 2020), but signals specific to certain shell portions (Ullmann *et al.*, 2017a) or types of shell layers (*e.g.*, Cusack *et al.*, 2008; Perez-Huerta *et al.*, 2008) are well documented and need to be taken into account.

Bivalves are the most complex group in terms of the fossil biominerals, because there are forms that secreted aragonite, calcite, or both carbonate polymorphs (Marin *et al.*, 2012; Yarra *et al.*, 2021). Where aragonite preservation can be established, primarily aragonitic fossils would be suitable targets for palaeoclimate work. However, in Mesozoic strata, calcitic forms are much more commonly sufficiently preserved for geochemical work, as expected from the relative difference in resistance to recrystallisation of these carbonate polymorphs under most conditions of diagenesis (Busenberg and Plummer, 1989). Particularly thick-shelled forms such as oysters (*e.g.*, Korte *et al.*, 2009; de Winter *et al.*, 2020; Price *et al.*, 2023) and the calcite parts of rudists (Steuber, 1996; de Winter *et al.*, 2021) have been used successfully. Bivalve habitats and degree of mobility are overall more complex than for brachiopods (*e.g.*, Hallam, 1976; Aberhan, 1994), and tolerance of some taxa to adverse environmental condition might be reflected in their shell geochemistry (Korte, Hesselbo, 2011). Therefore, awareness of the taxon-specific ecology may be important in specific cases. Ontogenetic drifts in incorporation of elements (Schöne *et al.*, 2011; Barrat *et al.*, 2023) is also known. Also isotope ratios – especially for carbon – may be biased in some shell portions, even though such biases, at least for oxygen, are not usually very pronounced (Gillikin *et al.*, 2007; McConnaughey, Gillikin, 2008; Curley *et al.*, 2023).

OBSERVED HETEROGENEITY WITHIN MACROFOSSIL DATASETS

The sample size and sample position for fossil materials determine data heterogeneity and may bias geochemical proxies, the latter not only due to admixture of poorly preserved material, but also due to the biomineralization processes. Besides any preservation issues, the high growth rate of macroinvertebrates means that shell material captures seasonally changing conditions in the environment, as well as the organisms' metabolic response to seasonality. Other factors that may be difficult to detect such as food supply, seasonal spawning, etc., potentially also impact geochemical signatures.

As illustrated above and powerfully shown with imaging and geochemical mapping techniques (*e.g.*, Bruckschen *et al.*, 1995; Barbin, 2000, 2013; de Winter, Claeys, 2017), macrofossils are generally not uniformly well preserved. Minimizing sample size and avoiding shell areas that have been found to be problematic are thus preferable to reduce the risk of including substantial quantities of altered material. However, clearly in doing so, the potential primary heterogeneity of the shell material will be amplified in resulting datasets. Comparatively few studies have specifically addressed the degree of heterogeneity in well-preserved macrofossil carbonate. While this sparsity of data can be compensated to some degree by work on modern analogues, for instance in brachiopods and bivalves, it is presently unclear to what degree generalisations can be made for extinct taxa from the available information without close extant relatives. Nevertheless, constraints on these aspects of interpretation are improving.

Datasets that are large enough to quantify primary heterogeneity in a statistically robust way for individual fossils, and that are based on quantitative geochemical analysis with good control on accuracy and precision, including both C and O isotope and element/Ca ratio determinations, are rare (but see Dutton *et al.*, 2007; Wierzbowski, Joachimski, 2009; Sørensen *et al.*, 2015; Ullmann *et al.*, 2015, 2020; Stevens *et al.*, 2017). Additionally, some studies exist that utilise electron beam and laser ablation techniques in conjunction with physical sample extraction for isotopic measurements (McArthur *et al.*, 2007), as well as secondary ion mass spectrometry (Hoffmann *et al.*, 2021).

Studies based on wet chemical analyses and gas source mass spectrometry typically make use of samples of a few milligrams of calcite. Variability of any analysed proxy in individual fossils in these studies significantly exceeds the analytical uncertainty of the measurements (Dutton *et al.*, 2007; Wierzbowski, Joachimski, 2009; Sørensen *et al.*, 2015; Ullmann *et al.*, 2015, 2020; Stevens *et al.*, 2017). While some of this heterogeneity may be related to comparatively small sample size, drifts and trends in proxies have been observed in fossils that relate to ontogenetic profiling (*e.g.*, Steuber, 1996; Dutton *et al.*, 2007; Ullmann *et al.*, 2015), so the degree of heterogeneity seen in ontogenetic profiles is to be expected when obtaining macrofossil data in general (compare also Veizer *et al.*, 1999; Dera *et al.*, 2011; Ullmann *et al.*, 2014; Bodin *et al.*, 2015; Korte *et al.*, 2015; Hesselbo *et al.*, 2020; Price *et al.*, 2023). Variability of published datasets looking at stratigraphic trends in carbon and oxygen isotopes and element/Ca ratios is in agreement with this prediction of the magnitude of inherent 'noise' in macrofossil datasets (Fig. 3).

Chemostratigraphic datasets for individual macrofossil groups in a basin typically show 2 s.d. variability of slightly less than 1‰ in $\delta^{18}O$, and somewhat higher variability in carbon isotope ratios. Variability in Mg/Ca ratios is typically around 30% (2 relative standard deviations) in such datasets, while variability in Sr/Ca is about 15%. In serially sampled macrofossils, the observed sample-to-sample variability is much reduced in belemnite rostra, where data show coherent trends over relatively easily resolved spatial scales, while similar datasets on individual bivalves only show a moderate reduction in variability as compared over stratigraphic datasets, perhaps related to slower shell secretion rates.

Where macrofossils are studied for chemostratigraphic purposes, this heterogeneity limits the size and confidence in the magnitude of perturbations in local water temperature and carbon cycle that can be resolved with such datasets. Where more robust trends in geochemical proxies are required, these have to be generated by averaging of data from multiple samples. For instance, there may be a tendency to overstate palaeotemperature change driven by extracting such magnitudes from maxima and minima in comparatively small macrofossil datasets, *e.g.*, 7–10°C for Early Toarcian warming based on brachiopods (Suan *et al.*, 2010). Stratigraphic changes in average macrofossil oxygen isotope ratios in the same interval and region are more suggestive of <4°C of warming (Ullmann *et al.*, 2020), with significant consequences for Earth system modeling based on palaeoclimate perturbations.

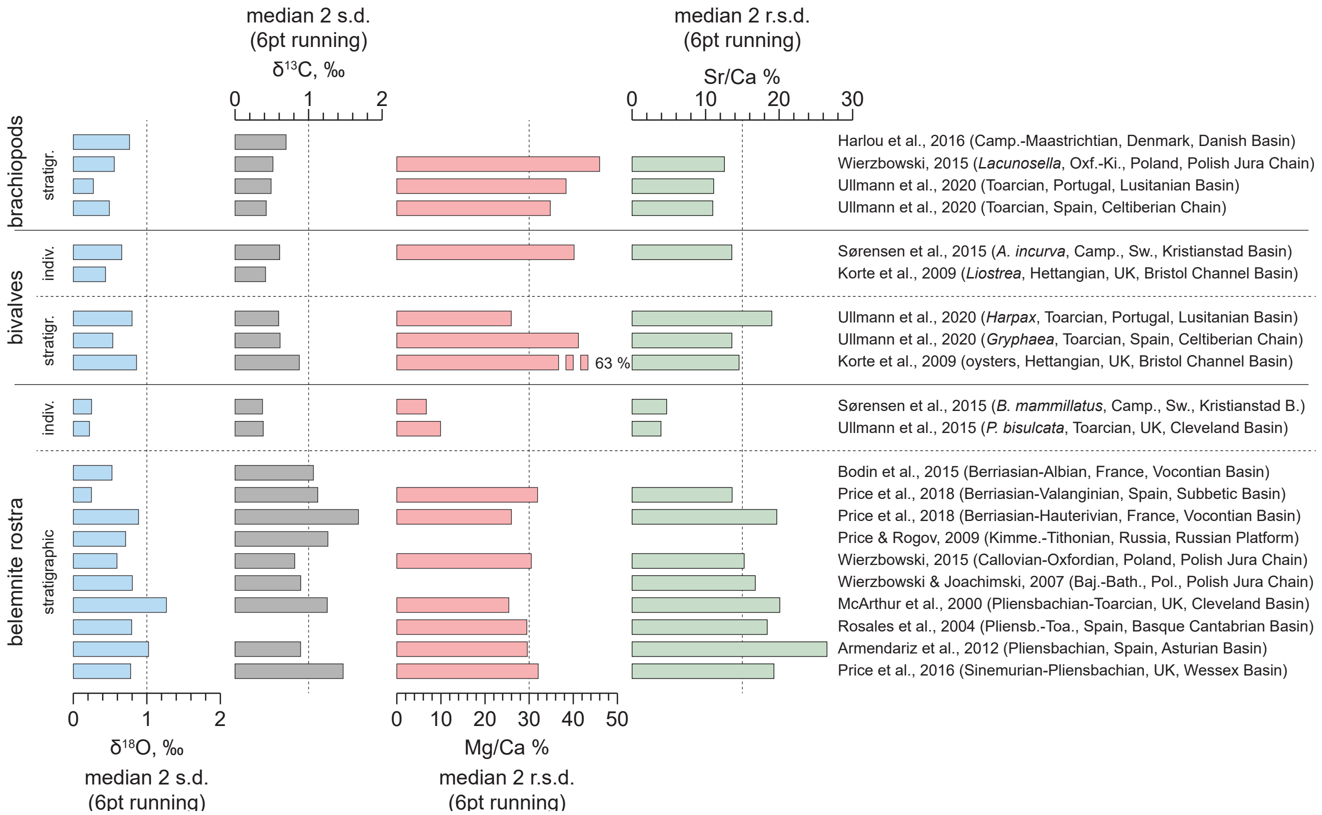

Fig. 3. Geochemical variability of published chemostratigraphic datasets and serial sampling of individual macrofossils across Jurassic and Cretaceous belemnites, bivalves, and brachiopods

Statistics are based on variability (2 standard deviations, s.d.) of ontogenetic profiles or chemostratigraphic trends. Stratigr. – stratigraphic; indiv. – Individual; Pliensb. – Pliensbachian; Toa. – Toarcian; Oxf. – Oxfordian; Ki. & Kimme. – Kimmeridgian; Camp. – Campanian; Pol. – Poland; Sw. – Sweden

GENERALISED SAMPLE ASSESSMENT AND SAMPLING PROCEDURES

GENERALISED PLANNING FOR A MACROFOSSIL-BASED STUDY

A general framework for assessing samples is outlined here to inform the layout of palaeoenvironmental studies and aid decisions on which fossil materials to target (Tab. 1). This assessment is qualitative, because it is recognized that assessments of a particular scenario will change over time as relevant aspects are continually re-evaluated, e.g. relating to biomineralisation.

All categories of this scheme outlined below (Tab. 2–8) impact on the contribution that a macrofossil-based study can make, where most of the time it will be the category that fares worst that defines the overall relevance of the study. However, the outcome of such an assessment has to be based on the current scientific context. A guiding principle might be that a study will be worth carrying out as long as it improves measurably on the current understanding of a particular problem.

Table 1

Evaluation matrix for assessment of relevant parameters influencing the reliability of macrofossil-based geochemical studies. Quality parameters from very high (A) to very low (F) are outlined below in text

Stratigraphic control	Depositional setting	Diagenetic constraints	Fossil type/ bio-mineralisation	Ecology	Taxonomy	Sample location
A	A	A	A	A	A	A
B	B	B	B	B	B	B
C	C	C	C	C	C	C
D	D	D	D	D	D	D
E	E	E	E	E	E	E
F	F	F	F	F	F	F

Stratigraphic control

Understanding Earth System evolution in detail requires robust and precise age control of input data, allowing correlation of datasets across large distances. Without these temporal constraints, even otherwise high-quality chemostratigraphic datasets will be of limited value.

Table 2

Evaluation scale for stratigraphic control on macrofossil age

A	Excellent stratigraphic control. Samples can be placed into chronostratigraphic context with certainty, e.g. via direct links to GSSP, type sections, and/or well established, calibrated marker bed numbers
B	Very good stratigraphic control. Samples can be placed into a robust stratigraphic framework that relates well to international chronostratigraphic chart, e.g. via well-constrained biostratigraphic schemes
C	Moderate-good stratigraphic control. Sample placement into stratigraphic framework is generally well-supported, but there are significant limitations, e.g. comparatively limited biostratigraphic constraints and resulting moderate uncertainty in placement of zonal boundaries
D	Moderate-poor stratigraphic control. Some relevant stratigraphic constraints exist, but they are generally limited, and perhaps of only regional significance, causing moderate to large uncertainty in the position of a sample in the chronostratigraphic scheme
E	Poor stratigraphic control. Stratigraphic constraints for the samples are very weak causing a high uncertainty in the placement in a wider stratigraphic context
F	Very poor stratigraphic control. Little to no stratigraphic constraint on the position of the sample in the chronostratigraphic chart

Depositional setting

Depositional settings can have major impacts on the expression of geochemical proxies, e.g. through changes in salinity, possible water mass stratification, and others factors impacting on the ability to utilize datasets for inferences on global palaeoclimates.

Table 3

Evaluation scale of controls on depositional environment

A	Excellent constraints on physical conditions at studied location such as water depth, salinity, oxygenation etc., allowing environmental parameters to be determined with high very high degree of confidence
B	Very good control on depositional environment. Knowledge about the depositional context allows very good constraints on parameters such as water depth, salinity, water oxygenation etc.
C	Moderate-good control on depositional environment. The depositional environment is generally well understood, but some ambiguity exists in relation of one or a few key parameters such as salinity, therefore placing some limitations on the interpretation potential of macrofossil-derived data
D	Moderate-poor control on depositional environment. The general depositional setting is known, but constraints on environmental parameters are comparatively weak, limiting the degree to which macrofossil data can be contextualized
E	Poor control on depositional environment. There is uncertainty in key parameters relating to the depositional setting that place severe limitations on the interpretations
F	Very poor control on depositional environment. There is major ambiguity over key parameters relating to the depositional setting making interpretations of geochemical data from fossil materials highly doubtful

Diagenetic constraints

One of the biggest hinderances in interpretation of macrofossil-based data is an incomplete understanding of the expression of diagenesis, and hence, whether (and to what degree) analytical results are offset from the primary values. Optimisation of knowledge about diagenetic trends for all proxies of interest is therefore paramount for studies of fossil geochemistry.

Table 4

Evaluation scale for diagenetic constraints

A	Excellent constraints on diagenesis. Diagenetic signatures are either homogeneous or stratigraphic changes and/or dependence on lithology and fossil type are very well constrained. Diagenesis is either insignificant due to exceptional fossil preservation, or compromised material can be easily identified via key geochemical proxies.
B	Very good control on diagenesis. Diagenetic signatures are quite uniform or stratigraphic changes and/or dependence on lithology and fossil type are well constrained. Diagenesis is either minor or compromised material can mostly confidently identified via key geochemical proxies.
C	Moderate-good constraints on diagenesis. Diagenetic signatures are somewhat complex due to multiple diagenetic events and/or somewhat heterogeneous composition of diagenetic endmembers which cannot easily be linked to stratigraphy, lithology or fossil type. Preservation of fossils is regularly good, and diagenetic overprints can largely be identified with a good degree of robustness using key geochemical proxies.
D	Moderate-poor constraints on diagenesis. Diagenetic signatures are complex, e.g. due to multiple diagenetic phases impacting on the fossils differentially. No clear diagenetic endmember can be identified. Fossil preservation is moderate and constraining the degree of overprint is not always possible based on common criteria.
E	Poor constraints on diagenesis. Diagenetic signatures are complex. Identification of diagenetic endmembers may not be possible and multiple diagenetic phases may have impacted on fossil preservation, but some inference about diagenetic trends are possible. Fossil preservation tends to be poor and no common criteria to identify well-preserved materials can be identified.
F	Very poor constraints on diagenesis. Diagenetic signatures are very complex and diagenetic endmembers either highly heterogeneous or not identifiable. Fossil preservation is mostly very poor and very few samples, if any, can be confidently identified as well preserved.

Fossil type and biomineralisation

Macrofossils require specific sampling approaches to target material that is least likely to be compromised by diagenetic overprints as well as enhanced expression of vital effects, either of which could lead to substantial bias on analytical outcomes.

Table 5

Evaluation scale for fossil type

A	Ideal fossil material for determination of target proxy. The fossil material is well understood and widely studied, including modern representatives of the target taxa, and has been found to incorporate the target proxy faithfully.
B	Very good fossil material for determination of target proxy. The fossil material is well understood and widely studied, including modern analogues of closely related taxa. There is good confidence that the target proxy can be faithfully extracted from this fossil type.
C	Moderate-good fossil material for determination of target proxy. The fossil material is reasonably well understood and/or widely studied, and there are reasonably good constraints on their biomineralisation from related modern taxa or through comparison with well-constrained fossils. There is good confidence that the fossil material is suitable for extraction of the target proxy, even though minor possible biases might exist.
D	Moderate-poor fossil material. The fossil type is incompletely understood and/or not commonly studied, and there may be significant challenges ground truthing data due to the absence of suitable modern analogues or other fossil material that proxy data can be calibrated against. Some biases imposed on the target proxy may be known.
E	Poor fossil material. The fossil type is incompletely understood and/or not commonly studied. There are substantial challenges in ground truthing proxy data or the target proxy is known to be significantly biased in the target material.
F	Very poor fossil material. There is very little understanding of the way that the target proxy is incorporated in the fossil shell and/or the fossil material may be barely studied if at all. There is little prospect of being able to ground truth the data and there may be no clear modern analogue to compare the fossil material with. Alternatively, the fossil type may be known to not faithfully record the target proxy.

Ecology

Ecological constraints are useful, as they allow contextualization of geochemical proxies in shell materials on the basis of inferences about habitat, feeding behaviour, metabolic rates, and many more factors.

Table 6

Evaluation scale for understanding of fossil ecology

A	The ecology of the target taxon is very well established, causing no complications for understanding the studied proxy. Transfer functions for the proxy consequently have negligible uncertainty, allowing for very precise and accurate palaeoenvironmental reconstruction.
B	The ecology of the target fossil is well known, causing little if any complexity for understanding the studied proxy. Transfer functions for the proxy have little uncertainty, allowing for precise and accurate palaeoenvironmental reconstruction.
C	The ecology of the target fossil is reasonably well known, or the ecology may impose some significant complexity for understanding the studied proxy. Some uncertainty on transfer functions for the proxy arise as a consequence. Palaeoenvironmental reconstruction is nevertheless possible with reasonably good confidence despite these limitations.
D	Some aspects of ecology are poorly established or cause considerable variability in the target proxy and therefore lead to considerable complexity for the understanding of the studied proxy. Palaeoenvironmental reconstruction is somewhat doubtful as a result, even though general inferences can be treated as robust.
E	The ecology is poorly known or known to be complex, causing substantial challenges for reconstructing palaeoenvironmental parameters. Use of this taxon does only allow for broad inferences about the target proxy.
F	The ecology is largely unknown or known to be highly complex. Palaeoenvironmental reconstructions are consequently highly doubtful for the target proxy.

Taxonomy

The expression of geochemical proxies and magnitude of vital effects can be highly specific to individual taxa, even though this is not necessarily the case. Nevertheless, the better the taxonomic control, the better the ability to assess the potential of taxon-specific expression of geochemical proxies and comparability to other published datasets.

Table 7

Evaluation scale for taxonomic control

A	The fossil is identified to species level, or it is known that the target proxy is not differentially expressed in the fossil type at a finer level than can be determined for the specimen.
B	The fossil is identified to genus level, or it is known that there is little differential expression in the target proxy in the fossil type at a finer level than can be determined for the specimen.
C	The fossil is identified to family level. The target proxy is mostly insensitive to finer taxonomic levels, but some minor differences in expression may occur.
D	Taxonomic identification of the fossil is coarse. The target proxy is reasonably uniformly expressed in this fossil type, so that general interpretations remain possible.
E	Taxonomic identification of the fossil is very coarse. The target proxy is known to be taxon specific, allowing only for general inferences.
F	Taxonomic identification of the fossil is very coarse. The target proxy is highly taxon specific, precluding meaningful interpretation of the data.

Sample location

The ability to control where a sample is taken on a fossil can be critical for the research outcome. Choice of sample location may be limited by the preservation of the fossil, but nevertheless should be monitored carefully in relation to known biomineralisation behaviour of the targeted substrate.

Table 8

Evaluation scale for sample position on fossil material

A	The sample can be taken from a shell portion for which it is known that the proxy is expressed without bias. Heterogeneity of the shell material is known to be of no consequence to the studied problem .
B	The sample can be taken from a shell portion where the proxy is known to be expressed without bias. Unwanted variability of the proxy is minimal.
C	The samples can be taken from a shell portion where the proxy is known to be almost unbiased. Unwanted variability in the expression of the proxy is limited.
D	The sample position is known to be sub-optimal as there is known, but limited bias on the target proxy. Unwanted variability in the expression of the proxy is considerable.
E	The sample position is known to affect the expression of the proxy considerably, causing significant bias on the outcome. Unwanted variability in the expression of the proxy is large.
F	The sample position is known to strongly affect proxy expression, making the data largely uninterpretable. Unwanted variability in the expression of the proxy makes extraction of meaningful information impossible.

SUSTAINABILITY AND MAXIMIZING DATA VALUE

Maintaining a geochemical laboratory and analytical instrumentation are inevitably detrimental to the environment, be it via the consumption of energy, the generation of chemical waste that needs disposal, or the requirements for specialist consumables and reagents such as clean sample containers, purified water and acids, and high purity gases. This issue is now widely acknowledged and has led to the establishment of various sustainability programs (*e.g.*, Schell, Bruns, 2024).

Guiding principles of research on Mesozoic macrofossils must therefore be to maximise the amount, accessibility, and utilization of data that are derived from relevant material, and to design laboratory protocols that limit the extent of environmental impact caused by the analytical work and required laboratory infrastructure as much as possible without compromising research outcomes.

This paradigm aligns with the ambition to increase the open accessibility of research and research data (Nosek *et al.*, 2015) and with the necessity to maximise metainformation about research samples to best ascertain that analytical data can be meaningfully interpreted.

Information about the quality and nature of macrofossil carbonate arises from numerous steps in preparation and analytical protocols, many of which are not commonly reported, if they are utilized at all. In particular, reporting of sample location and sample weight as well as descriptive information about the nature of the studied material can be critical to contextualise findings and should be included into data reports. Maintaining gravimetric control on sample masses and dilution factors, for instance, allows the carbonate content of samples to be determined using various analytical instruments (Ullmann *et al.*, 2020), a measure that can be taxon specific and complementary for interpretation of taxonomic and ecological parameters in fossil populations.

Even though some analytical data may not be utilized for interpretative work in a study, full disclosure of all acquired research data in an easily editable format is highly encouraged to allow these outcomes to be available for future research.

GENERALISED SAMPLING PROCEDURE

Based on the above considerations regarding sample preservation, diagenesis, and heterogeneity of fossil materials, and the need to constrain fossil preservation as comprehensively as possible, the following general sampling and analytical procedure is proposed (Fig. 4). This schematic protocol has to be adapted to the specific requirements of the

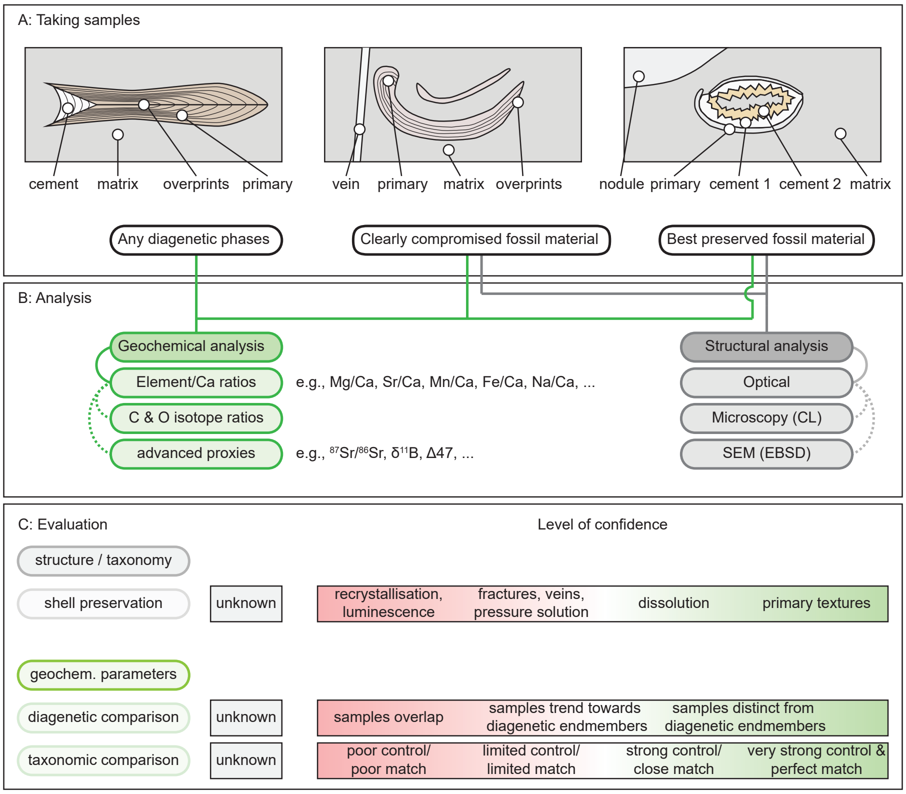

Fig. 4: Generalized sampling, analysis and evaluation procedure for Mesozoic macrofossils

A. Sampling of fossil materials should include poorly preserved material as well as diagenetic and bulk phases to be able to constrain post-depositional overprints. Sampling for structural assessment of hard parts is advised for fossil materials, ideally including also poorly preserved parts. **B.** Geochemical analyses should be undertaken on all samples, covering all proxies of interest for diagenetic phases, poorly preserved and best-preserved material, determining as a minimum element concentrations supporting the interpretation of preservation state and – in the case of fossil materials – also at least basic study of optical evaluation of preservation. **C.** Evaluation of obtained results should address level of structural and geochemical preservation of hard parts, based on the best achievable constraints from diagenetic endmembers and published data on comparable taxa

accessible fossil substrates and target proxies, keeping in mind the specific constraints from studied successions and fossil types.

Following the selection of a section/core/collection with optimal stratigraphic control and knowledge about depositional environment, sampling, as outlined above, ideally involves all relevant diagenetic phases that are observable in studied successions, and also fossil materials that are compromised by overprints. This approach allows attribution of geochemical trends of alteration to specific diagenetic phases, and evaluation of the direction and magnitudes of overprint.

Upon determination of the chosen fossil substrate to the finest possible taxonomic level, sample extraction needs to be done in line with the specific requirements of this fossil type, with the aim to minimize sample size which is dictated by the targeted proxies. In any case, the location of sampling and sample size should be noted to contextualize later outcomes. This approach allows to extract materials that are least likely to be affected by diagenetic overprints or otherwise compromised by uncontrollable biological factors.

Sampling procedures should always include optical assessment of preservation, at least by eye, but ideally also using binocular microscope, petrographic microscope or more sophisticated methodology that allows for the visualization of the preservation of individual crystal units such as shell fibres in the fossil carbonate. Where geochemical proxies are targeted, the target proxy of choice and concentrations of a basic set of elements such as Mg, Sr, Mn and Fe should be determined for the fossil material as well as on samples of compromised fossil material as well as relevant diagenetic phases.

Comparison of results from best preserved samples with compromised samples and diagenetic endmembers allows best constraint on which diagenetic phase may have impacted geochemical signatures most prominently, and to quantify the degrees of overprint on materials targeted for palaeoenvironmental or chemostratigraphic interpretation. This knowledge in turn helps to determine if quantitative markers for preservation can be set for specimens or fossil groups in the studied section, which may well be specific to taxon, stratigraphic level, lithology, and target proxy.

Data that pass such rigorous screening can then be confidently considered to best reflect the primary signals locked into the carbonate during biomineral secretion and interpreted in relation to palaeoenvironments, keeping in mind the complicating factors arising from biological control on the formation of these materials.

CONCLUSIONS

Macrofossil carbonate constitutes one of the most important substrates for the reconstruction of Mesozoic palaeoenvironments and chemostratigraphy. To optimize the reliability of results obtained, some general principles of sampling and analysis are proposed.

Samples should be taken from best preserved fossil materials, but also from visibly altered materials and other clearly diagenetic phases in the studied succession, at the same time minimizing sample size for best-preserved fossil materials.

Samples should be described by comprehensive metainformation, including stratigraphic level, sample position on fossil hard part, and sample size, and the data reported in full.

Sample evaluation should include optical and geochemical features of studied specimens and be linked to geochemical signatures of compromised fossil material and diagenetic endmembers. Comparison to reported geochemical and structural information on taxa as closely linked as possible in time and taxonomy will assist this evaluation.

A hierarchical assessment protocol should be adopted, where samples for advanced proxies are supported by analytical data covering at least basic chemical composition.

Acknowledgments. The ideas presented in this work benefitted strongly from discussions with many colleagues, including Grzegorz Pieńkowski, who did not shy away from challenging established hypotheses about the Mesozoic Earth environment and often catalysed new interpretations as a consequence. Many thanks go to Stephen P. Hesselbo for his detailed editorial work, Jacek Grabowski, as well as Hubert Wierzbowski and an anonymous reviewer, helping to greatly improve the clarity of this contribution.

REFERENCES

ABERHAN M., 1994 – Guild-structure and evolution of Mesozoic benthic shelf communities. *Palaios*, **9**, 6: 516–545, doi: https://doi.org/10.2307/3515126.

AL-AASM I.S., VEIZER J., 1982 – Chemical stabilization of low-Mg calcite; an example of brachiopods. *Journal of Sedimentary Research*, **52**, 1101–1109.

AL-AASM I.S., VEIZER J., 1986a – Diagenetic stabilization of aragonite and low-Mg calcite; I, Trace elements in rudists. *Journal of Sedimentary Research*, **56**, 1: 138–152, doi: https://doi.org/10.1306/212F88A5-2B24-11D7-8648000102C1865D.

AL-AASM I.S., VEIZER J., 1986b – Diagenetic stabilization of aragonite and low-Mg calcite; II, Stable isotopes in rudists. *Journal of Sedimentary Research*, **56**, 6: 763–770, doi: https://doi.org/10.2110/jsr.56.763.

ALBERTI M., FÜRSICH F.T., ANDERSEN N., 2019 – First steps in reconstructing Early Jurassic sea water temperatures in the Andean Basin of northern Chile based on stable isotope analyses of oyster and brachiopod shells. *Journal of Palaeogeography*, **8**, 1: 1–17, doi: https://doi.org/10.1186/s42501-019-0048-0.

ALMEIDA M.J., MACHADO J., MOURA G., AZEVEDO M., COIMBRA J., 1998 – Temporal and local variations in biochemical composition of Crassostrea gigas shells. *Journal of Sea Research*, **40**, 3/4: 233–249, doi: https://doi.org/10.1016/S1385-1101(98)00033-1.

ANGIOLINI L., DARBYSHIRE D.P.F., STEPHENSON M.H., LENG M.J., BREWER T.S., BERRA F., JADOUL F., 2007 – Lower Permian brachiopods from Oman: their potential as climatic proxies. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, **98**, 3/4: 327–344, doi: https://doi.org/10.1017/S1755691008075634.

ARMENDÁRIZ M., ROSALES I., BÁDENAS B., AURELL M., GARCÍA-RAMOS J.C., PIÑUELA L., 2012 – High-resolution chemostratigraphic records from Lower Pliensbachian belemnites: Palaeoclimatic perturbations, organic facies and water mass exchange (Asturian basin, northern Spain). *Palaeogeography, Palaeoclimatology, Palaeoecology*, **333/334**: 178–191, https://doi.org/10.1016/j.palaeo.2012.03.029.

AUCLAIR A.C., JOACHIMSKI M.M., LÉCUYER C., 2003 – Deciphering kinetic, metabolic and environmental controls on stable isotope fractionations between seawater and the shell of Terebratalia transversa (Brachiopoda). *Chemical Geology*, **202**, 1/2: 59–78, doi: https://doi.org/10.1016/S0009-2541(03)00233-X.

BAILEY T.R., ROSENTHAL Y., MCARTHUR J.M., van de SCHOOTBRUGGE B., THIRLWALL M.F., 2003 – Paleoceanographic changes of the Late Pliensbachian–Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event. *Earth and Planetary Science Letters*, **212**, 3/4: 307–320, doi: https://doi.org/10.1016/S0012-821X(03)00278-4.

BAJNAI D., GUO W., SPÖTL C., COPLEN T.B., METHNER K., LÖFFLER N., KRSNIK E., GISCHLER E., HANSEN M., HENKEL D., PRICE G.D., 2020 – Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures. *Nature Communications*, **11**, 1: 4005, doi: https://doi.org/10.1038/s41467-020-17501-0.

BANNER J.L., HANSON G.N., 1990 – Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta*, **54**, 11: 3123–3137, doi: https://doi.org/10.1016/0016-7037(90)90128-8.

BARBIN V., 2000 – Cathodoluminescence of carbonate shells: biochemical vs diagenetic process. In Cathodoluminescence in geosciences (pp. 303–329). Berlin, Heidelberg: Springer Berlin Heidelberg.

BARBIN V., 2013 – Application of cathodoluminescence microscopy to recent and past biological materials: a decade of progress. *Mineralogy and Petrology*, **107**: 353–362.

BARBIN V., RAMSEYER K., ELFMAN M., 2008 – Biological record of added manganese in seawater: a new efficient tool to mark in vivo growth lines in the oyster species Crassostrea gigas. *International Journal of Earth Sciences*, **97**: 193–199, doi: https://doi.org/10.1007/s00531-006-0160-0.

BARRAT J.A., CHAUVAUD L., OLIVIER F., POITEVIN P., ROUGET M.L., 2023 – Trace elements in bivalve shells: How "vital effects" can bias environmental studies. *Chemical Geology*, **638**: 121695, doi: https://doi.org/10.1016/j.chemgeo.2023.121695.

BODIN S., MEISSNER P., JANSSEN N.M.M., STEUBER T., MUTTERLOSE J., 2015 – Large igneous provinces and organic carbon burial: Controls on global temperature and continental weathering during the Early Cretaceous. *Global and Planetary Change,* **133**: 238–253, doi: http://dx.doi.org/10.1016-/j.gloplacha.2015.09.001.

BOWEN R., 1960 – Paleotemperature analyses of Mesozoic Belemnoidea from Germany and Poland. *The Journal of Geology*, **69**, 1: 75–83, doi: https://doi.org/10.1086/626716.

BOWEN R., FRITZ P., 1963 – Oxygen isotope paleotemperature analyses of Lower and Middle Jurassic fossils from Pliensbach, Württemberg (Germany). *Experientia*, **10**: 461–465, doi: https://doi.org/10.1007/BF02150647.

BRAND U., 1991 – Strontium isotope diagenesis of biogenic aragonite and low-Mg calcite. *Geochimica et Cosmochimica Acta*, **55**, 2: 505–513, doi: https://doi.org/10.1016/0016-7037(91)90008-S.

BRAND U., VEIZER J., 1980 – Chemical diagenesis of a multicomponent carbonate system; 1, Trace elements. *Journal of Sedimentary Research*, **50**, 4: 1219–1236, doi: https://doi.org/10.1306/212F7BB7-2B24-11D7-8648000102C1865D.

BRAND U., VEIZER J., 1981 – Chemical diagenesis of a multicomponent carbonate system; 2, Stable isotopes. *Journal of Sedimentary Research*, **51**, 3: 987–997, doi: https://doi.org/10.1306/212F7DF6-2B24-11D7-8648000102C1865D.

BRAND U., LOGAN A., HILLER N., RICHARDSON J., 2003 – Geochemistry of modern brachiopods: applications and implications for oceanography and paleoceanography. *Chemical Geology*, **198**, 3/4: 305–334, doi: https://doi.org/10.1016/S0009-2541(03)00032-9.

BRAND U., WEBSTER G.D., AZMY K., LOGAN A., 2007 – Bathymetry and productivity of the southern Great Basin seaway, Nevada, USA: An evaluation of isotope and trace element chemistry in mid-Carboniferous and modern brachiopods. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **256**, 3/4: 273–297, doi: https://doi.org/10.1016/j.palaeo.2007.02.034.

BRAND U., AZMY K., TAZAWA J.I., SANO H., BUHL D., 2010 – Hydrothermal diagenesis of Paleozoic seamount carbonate components. *Chemical Geology*, **278**, 3/4: 173–185, doi: https://doi.org/10.1016/j.chemgeo.2010.09.010.

BRAND U., JIANG G., AZMY K., BISHOP J., MONTAÑEZ I.P., 2012 – Diagenetic evaluation of a Pennsylvanian carbonate succession (Bird Spring Formation, Arrow Canyon, Nevada, USA) – 1: Brachiopod and whole rock comparison. *Chemical Geology*, **308**: 26–39, doi: https://doi.org/10.1016/j.chemgeo.2012.03.017.

BRAND U., AZMY K., BITNER M.A., LOGAN A., ZUSCHIN M., CAME R., RUGGIERO E., 2013 – Oxygen isotopes and $MgCO_3$ in brachiopod calcite and a new paleotemperature equation. *Chemical Geology*, **359**: 23–31, doi: https://doi.org/10.1016/j.chemgeo.2013.09.014.

BRUCKSCHEN P., BRUHN F., MEIJER J., STEPHAN A., VEIZER J., 1995 – Diagenetic alteration of calcitic fossil shells: Proton microprobe (PIXE) as a trace element tool. *Nuclear Instruments and Methods in Physics Research B*, **104**: 427–431.

BUSENBERG E., PLUMMER L.N., 1989 – Thermodynamics of magnesian calcite solid-solutions at 25 C and 1 atm total pressure. *Geochimica et Cosmochimica Acta*, **53**, 6: 1189–1208, doi: https://doi.org/10.1016/0016-7037(89)90056-2.

BUTLER P.G., WANAMAKER JR. A.D., SCOURSE J.D., RICHARDSON C.A., REYNOLDS D.J., 2013 – Variability of marine climate on the North Icelandic Shelf in a 1357-year proxy archive based on growth increments in the bivalve *Arctica islandica*. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **373**: 141–151, doi: https://doi.org/10.1016/j.palaeo.2012.01.016.

CARLSON S.J., 2016 – The evolution of Brachiopoda. *Annual Review of Earth and Planetary Sciences*, **44**: 409–438, doi: https://doi.org/10.1146/annurev-earth-060115-012348.

CARPENTER S.J., LOHMANN K.C., 1992 – SrMg ratios of modern marine calcite: Empirical indicators of ocean chemistry and precipitation rate. *Geochimica et Cosmochimica Acta*, **56**, 5: 1837–1849, doi: https://doi.org/10.1016/0016-7037(92)90314-9.

CARPENTER S.J., LOHMANN K.C., 1995 – $\delta^{18}O$ and $\delta^{13}C$ values of modern brachiopod shells. *Geochimica et Cosmochimica Acta*, **59**, 18: 3749–3764, doi: https://doi.org/10.1016/0016-7037(95)00291-7.

CASELLA L.A., GRIESSHABER E., RODA M.S., ZIEGLER A., MAVROMATIS V., HENKEL D., LAUDIEN J., HÄUSSERMANN V., NEUSER R.D., ANGIOLINI L., DIETZEL M., 2018 – Micro- and nanostructures reflect the degree of diagenetic alteration in modern and fossil brachiopod shell calcite: a multi-analytical screening approach (CL, FE-SEM, AFM, EBSD). *Palaeogeography, Palaeoclimatology, Palaeoecology*, **502**: 13–30, doi: https://doi.org/10.1016/j.palaeo.2018.03.011.

CHAVE K.E., 1954 – Aspects of the biogeochemistry of magnesium 1. Calcareous marine organisms. *The Journal of Geology*, **62**, 3: 266–283, doi: https://doi.org/10.1086/626162.

CHECA A.G., 2018 – Physical and biological determinants of the fabrication of molluscan shell microstructures. *Frontiers in Marine Science*, **5**: 353, doi: https://doi.org/10.3389/fmars.2018.00353.

CHECA A.G., ESTEBAN-DELGADO F.J., RODRÍGUEZ-NAVARRO A.B., 2007 – Crystallographic structure of the foliated calcite of bivalves. *Journal of Structural Biology*, **157**, 2: 393–402, doi: https://doi.org/10.1016/j.jsb.2006.09.005.

COGGON R.M., TEAGLE D.A., SMITH-DUQUE C.E., ALT J.C., COOPER M.J., 2010 – Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins. *Science*, **327**, 5969: 1114–1117, doi: https://doi.org/10.1126/science.1182252.

COMPSTON W., 1960 – The carbon isotopic compositions of certain marine invertebrates and coals form the Australian Permian. *Geochimica et Cosmochimica Acta*, **18**: 1–22, doi: https://doi.org/10.1016/0016-7037(60)90013-2.

CRAVO A., FOSTER P., ALMEIDA C., COMPANY R., COSSON R.P., BEBIANNO M.J., 2007 – Metals in the shell of Bathymodiolus azoricus from a hydrothermal vent site on the Mid-Atlantic Ridge. *Environment international*, **33**, 5: 609–615, doi: https://doi.org/10.1016/j.envint.2007.01.002.

CURLEY A.N., PETERSEN S.V., EDIE S.M., GUO W., 2023 – Biologically driven isotopic fractionations in bivalves: from palaeoenvironmental problem to palaeophysiological proxy. *Biological Reviews*, **98**: 1013–1032, doi: https://doi.org/10.1111/brv.12940.

CURTIS C.D., KRINSLEY D., 1965 – The detection of minor diagenetic alteration in shell material. *Geochimica et Cosmochimica Acta*, **29**, 2: 71–84, doi: https://doi.org/10.1016/0016-7037(65)90118-3.

CUSACK M., 2016 – Biomineral electron backscatter diffraction for palaeontology. *Palaeontology*, **59**, 2: 171–179, doi: https://doi.org/10.1111/pala.12222.

CUSACK M., PÉREZ-HUERTA A., JANOUSCH M., FINCH A.A., 2008 – Magnesium in the lattice of calcite-shelled brachiopods. *Chemical Geology*, **257**, 1/2: 59–64, doi: https://doi.org/10.1016/j.chemgeo.2008.08.007.

DERA G., BRIGAUD B., MONNA F., LAFFONT R., PUCÉAT E., DECONINCK J.F., PELLENARD P., JOACHIMSKI M.M., DURLET C., 2011 – Climatic ups and downs in a disturbed Jurassic world. *Geology*, **39**, 3: 215–218, doi: https://doi.org/10.1130/G31579.1.

de WINTER N.J., CLAEYS P., 2017 – Micro X-ray fluorescence (µXRF) line scanning on Cretaceous rudist bivalves: A new method for reproducible trace element profiles in bivalve calcite. *Sedimentology*, **64**, 231–251. doi: https://doi.org/10.1111/sed.12299.

de WINTER N.J., ULLMANN C.V., SØRENSEN A.M., THIBAULT N., GODERIS S., Van MALDEREN S.J., SNOECK C., GOOLAERTS S., VANHAECKE F., CLAEYS P., 2020 – Shell chemistry of the boreal Campanian bivalve *Rastellum diluvianum* (Linnaeus, 1767) reveals temperature seasonality, growth rates and life cycle of an extinct Cretaceous oyster. *Biogeosciences*, **17**, 11: 2897–2922, doi: https://doi.org/10.5194/bg-17-2897-2020.

de WINTER N.J., MÜLLER I.A., KOCKEN I.J., THIBAULT N., ULLMANN C.V., FARNSWORTH A., LUNT D.J., CLAEYS P., ZIEGLER M., 2021 – Absolute seasonal temperature estimates from clumped isotopes in bivalve shells suggest warm and variable greenhouse climate. *Communications Earth & Environment*, **2**, 1: 121, doi: https://doi.org/10.1038/s43247-021-00193-9.

DODD J.R., 1967 – Magnesium and strontium in calcareous skeletons: a review. *Journal of Paleontology*, **41**, 6: 1313–1329.

DUTTON A., HUBER B.T., LOHMANN K.C., ZINSMEISTER W.J., 2007 – High-resolution stable isotope profiles of a dimitobelid belemnite: implications for paleodepth habitat and late Maastrichtian climate seasonality. *Palaios*, **22**, 6: 642–650, doi: https://doi.org/10.2110/palo.2005.p05-064r.

EMILIANI C., 1954 – Temperatures of Pacific bottom waters and polar superficial waters during the Tertiary. *Science*, **119**, 3103: 853–855.

EMILIANI C., 1955 – Pleistocene temperatures. *Journal of Geology*, **63**, 6: 538–578, doi: https://doi.org/10.1086/626295.

ENGLAND J., CUSACK M., PATERSON N.W., EDWARDS P., LEE M.R., MARTIN R., 2006 – Hyperspectral cathodoluminescence imaging of modern and fossil carbonate shells. *Journal of Geophysical Research*, **111**, G03001. doi: https://doi.org/10.1029/2005JG000144.

FANTLE M.S., MAHER K.M., DEPAOLO D.J., 2010 – Isotopic approaches for quantifying the rates of marine burial diagenesis. *Reviews of Geophysics*, **48**, 3: RG3002, doi: https://doi.org/10.1029/2009RG000306.

FERNANDEZ A., KORTE C., ULLMANN C.V., LOOSER N., WOHLWEND S., BERNASCONI S.M., 2021 – Reconstructing the magnitude of Early Toarcian (Jurassic) warming using the reordered clumped isotope compositions of belemnites. *Geochimica et Cosmochimica Acta*, **293**: 308–327, doi: https://doi.org/10.1016/j.gca.2020.10.005.

FERREIRA J., MATTIOLI E., SUCHÉRAS-MARX B., GIRAUD F., DUARTE L.V., PITTET B., SUAN G., HASSLER A., SPANGENBERG J.E., 2019 – Western Tethys early and Middle Jurassic calcareous nannofossil biostratigraphy. *Earth-Science Reviews*, **197**: 102908, doi: https://doi.org/10.1016/j.earscirev.2019.102908.

FREITAS P.S., CLARKE L.J., KENNEDY H., RICHARDSON C.A., ABRANTES F., 2006 – Environmental and biological controls on elemental (Mg/Ca, Sr/Ca and Mn/Ca) ratios in shells of the king scallop *Pecten maximus*. *Geochimica et Cosmochimica Acta*, **70**, 20: 5119–5133, doi: https://doi.org/10.1016/j.gca.2006.07.029.

FREITAS P.S., CLARKE L.J., KENNEDY H., RICHARDSON C.A., 2016 – Manganese in the shell of the bivalve *Mytilus edulis*: seawater Mn or physiological control? *Geochimica et Cosmochimica Acta*, **194**: 266–278, doi: https://doi.org/10.1016/j.gca.2016.09.006.

FUJIOKA H., TAKAYANAGI H., YAMAMOTO K., IRYU Y., 2019 – The effects of meteoric diagenesis on the geochemical composition and microstructure of Pliocene fossil *Terebratalia coreanica* and *Laqueus rubellus* brachiopod shells from northeastern Japan. *Progress in Earth and Planetary Science*, **6**, 1: 1–23, doi: https://doi.org/10.1186/s40645-019-0289-7.

GILLIKIN D.P., LORRAIN A., MENG L., DEHAIRS F., 2007 – A large metabolic carbon contribution to the δ^{13}C record in marine aragonitic bivalve shells. *Geochimica et Cosmochimica Acta*, **71**, 12: 2936–2946, doi: https://doi.org/10.1016/j.gca.2007.04.003.

GODET A., DURLET C., SPANGENBERG J.E., FÖLLMI K.B., 2016 – Estimating the impact of early diagenesis on isotope records in shallow-marine carbonates: A case study from the Urgonian Platform in western Swiss Jura. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **454**: 125–138, doi: https://doi.org/10.1016/j.palaeo.2016.04.029.

GRÖCKE D.R., HESSELBO S.P., FINDLAY D.J., 2007 – Atypical diagenetic effects on strontium-isotope composition of Early Jurassic belemnites, Queen Charlotte Islands, British Columbia, Canada. *Canadian Journal of Earth Sciences*, **44**, 2: 181–197, https://doi.org/10.1139/e06-087.

GUO Y., DENG W., WEI G., 2019 – Kinetic effects during the experimental transition of aragonite to calcite in aqueous solution: Insights from clumped and oxygen isotope signatures. *Geochimica et Cosmochimica Acta*, **248**: 210–230, doi: https://doi.org/10.1016/j.gca.2019.01.012.

HALLAM A., 1976 – Stratigraphic distribution and ecology of European Jurassic bivalves. *Lethaia*, **9**, 3: 245–259, https://doi.org/10.1111/j.1502-3931.1976.tb01317.x.

HARLOU R., ULLMANN C.V., KORTE C., LAURIDSEN B.W., SCHOVSBO N.H., SURLYK F., THIBAULT N., STEMMERIK L., 2016 – Geochemistry of Campanian–Maastrichtian brachiopods from the Rørdal-1 core (Denmark): Differential responses to environmental change and diagenesis. *Chemical Geology*, **442**: 35–46, doi: https://doi.org/10.1016/j.chemgeo.2016.08.039.

HENKES G.A., PASSEY B.H., GROSSMAN E.L., SHENTON B.J., PÉREZ-HUERTA A., YANCEY T.E., 2014 – Temperature limits for preservation of primary calcite clumped isotope paleotemperatures. *Geochimica et Cosmochimica Acta*, **139**: 362–382, doi: https://doi.org/10.1016/j.gca.2014.04.040.

HESSELBO S.P., KORTE C., ULLMANN C.V., EBBESEN A.L., 2020 – Carbon and oxygen isotope records from the southern Eurasian Seaway following the Triassic-Jurassic boundary: Parallel long-term enhanced carbon burial and seawater warming. *Earth-Science Reviews*, **203**: 103131, doi: https://doi.org/10.1016/j.earscirev.2020.103131.

HOFFMANN R., STEVENS K., 2020 – The palaeobiology of belemnites–foundation for the interpretation of rostrum geochemistry. *Biological Reviews*, **95**, 1: 94–123, doi: https://doi.org/10.1111/brv.12557.

HOFFMANN R., RICHTER D.K., NEUSER R.D., JÖNS N., LINZMEIER B.J., LEMANIS R.E., FUSSEIS F., XIAO X., IMMENHAUSER A., 2016 – Evidence for a composite organic–inorganic fabric of belemnite rostra: Implications for palaeoceanography and palaeoecology. *Sedimentary Geology*, **341**: 203–215, doi: https://doi.org/10.1016/j.sedgeo.2016.06.001.

HOFFMANN R., LINZMEIER B.J., KITAJIMA K., NEHRKE G., DIETZEL M., JÖNS N., STEVENS K., IMMENHAUSER A., 2021 – Complex biomineralization pathways of the belemnite rostrum cause biased paleotemperature estimates. *Minerals*, **11**, 12: 1406, doi: https://doi.org/10.3390/min11121406.

HUCK S., HEIMHOFER U., 2021 – Early Cretaceous sea surface temperature evolution in subtropical shallow seas. *Scientific reports*, **11**, 1: 19765, doi: https://doi.org/10.1038/s41598-021-99094-2.

IMMENHAUSER A., SCHÖNE B.R., HOFFMANN R., NIEDERMAYR A., 2016 – Mollusc and brachiopod skeletal hard parts: Intricate archives of their marine environment. *Sedimentology*, **63**, 1: 1–59, doi: https://doi.org/10.1111/sed.12231.

JELBY M.E., THIBAULT N., SURLYK F., ULLMANN C.V., HARLOU R., KORTE C., 2014 – The lower Maastrichtian Hvidskud succession, Møns Klint, Denmark: calcareous nannofossil biostratigraphy, carbon isotope stratigraphy, and bulk and brachiopod oxygen isotopes. *Bulletin of the Geological Society of Denmark*, **62**, 89: p.e104.

JENKYNS H.C., 2010 – Geochemistry of oceanic anoxic events. *Geochemistry, Geophysics, Geosystems*, **11**, 3: Q03004, doi: https://doi.org/10.1029/2009GC002788.

JENKYNS H.C., MACFARLANE S., 2022 – The chemostratigraphy and environmental significance of the Marlstone and Junction Bed (Beacon Limestone, Toarcian, Lower Jurassic, Dorset, UK). *Geological Magazine*, **159**, 3: 357–371, doi: https://doi.org/10.1017/S0016756821000972.

JENKYNS H.C., JONES C.E., GRÖCKE D.R., HESSELBO S.P., PARKINSON D.N., 2002 – Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *Journal of the Geological Society*, **159**, 4: 351–378, doi: https://doi.org/10.1144/0016-764901-130.

JONES D.S., 1983 – Sclerochronology: reading the record of the molluscan shell: annual growth increments in the shells of bivalve molluscs record marine climatic changes and reveal surprising longevity. *American Scientist*, **71**, 4: 384–391.

JONES D.S., ALLMON W.D., 1995 – Records of upwelling, seasonality and growth in stable-isotope profiles of Pliocene mollusk shells from Florida. *Lethaia*, **28**, 1: 61–74, doi: https://doi.org/10.1111/j.1502-3931.1995.tb01593.x.

KORTE C., HESSELBO S.P., 2011 – Shallow marine carbon and oxygen isotope and elemental records indicate icehouse-greenhouse cycles during the Early Jurassic. *Paleoceanography*, **26**, 4: PA4219, doi: https://doi.org/10.1029/2011PA002160.

KORTE C., HESSELBO S.P., JENKYNS H.C., RICKABY R.E., SPÖTL C., 2009 – Palaeoenvironmental significance of carbon-and oxygen-isotope stratigraphy of marine Triassic–Jurassic boundary sections in SW Britain. *Journal of the Geological Society*, **166**, 3: 431–445, doi: https://doi.org/10.1144/0016-76492007-177.

KORTE C., HESSELBO S.P., ULLMANN C.V., DIETL G., RUHL M., SCHWEIGERT G., THIBAULT T., 2015 – Jurassic climate mode governed by ocean gateway. *Nature Communications*, **6**: 10015, doi: https://10.1038/ncomms10015.

LI Q., McARTHUR J.M., THIRLWALL M.F., TURCHYN A.V., PAGE K., BRADBURY H.J., WEIS R., LOWRY D., 2021 – Testing for ocean acidification during the Early Toarcian using $\delta^{44/40}$Ca and $\delta^{88/86}$Sr. *Chemical Geology*, **574**: 120228, doi: https://doi.org/10.1016/j.chemgeo.2021.120228.

LONGINELLI A., 1969 – Oxygen-18 variations in belemnite guards. *Earth and Planetary Science Letters*, **7**, 2: 209–212, doi: https://doi.org/10.1016/0012-821X(69)90038-7.

LOWENSTAM H.A., 1961 – Mineralogy, O^{18}/O^{16} ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans. *The Journal of Geology*, **69**, 3: 241–260, doi: https://doi.org/10.1086/626740.

MARIN F., LE ROY N., MARIE B., 2012 – The formation and mineralization of mollusk shell. *Frontiers in Bioscience-Scholar*, **4**, 3: 1099–1125, doi: https://doi.org/10.2741/S321.

MARSHALL J.D., 1992 – Climatic and oceanographic isotopic signals from the carbonate rock record and their preservation. *Geological Magazine*, **129**, 143–160.

MARTIN P.A., LEA D.W., 2002 – A simple evaluation of cleaning procedures on fossil benthic foraminiferal Mg/Ca. *Geochemistry, Geophysics, Geosystems*, **3**, 10: 8401, doi: https://doi.org/10.1029/2001GC000280.

McARTHUR J.M., DONOVAN D.T., THIRLWALL M.F., FOUKE B.W., MATTEY D., 2000 – Strontium isotope profile of the early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belemnite palaeotemperatures. *Earth and Planetary Science Letters*, **179**: 269–285.

McARTHUR J.M., MUTTERLOSE J., PRICE G.D., RAWSON P.F., RUFFELL A., THIRLWALL M.F., 2004 – Belemnites of Valanginian, Hauterivian and Barremian age: Sr-isotope stratigraphy, composition (^{87}Sr/^{86}Sr, δ^{13}C, δ^{18}O, Na, Sr, Mg), and palaeo-oceanography. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **202**, 3/4: 253–272, doi: https://doi.org/10.1016/S0031-0182(03)00638-2.

McARTHUR J.M., DOYLE P., LENG M.J., REEVES K., WILLIAMS C.T., GARCIA-SANCHEZ R., HOWARTH R.J., 2007 – Testing palaeo-environmental proxies in Jurassic belemnites: Mg/Ca, Sr/Ca, Na/Ca, δ^{18}O and δ^{13}C. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **252**, 3/4: 464–480, doi: https://doi.org/10.1016/j.palaeo.2007.05.006.

McCONNAUGHEY T., 1989 – ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochimica et Cosmochimica Acta*, **53**, 1: 151–162, doi: https://doi.org/10.1016/0016-7037(89)90282-2.

McCONNAUGHEY T.A., GILLIKIN D.P., 2008 – Carbon isotopes in mollusk shell carbonates. *Geo-Marine Letters*, **28**: 287–299, doi: https://doi.org/10.1007/s00367-008-0116-4.

METTAM C., JOHNSON A.L.A., NUNN E.V., SCHÖNE B.R., 2014 – Stable isotope (δ^{18}O and δ^{13}C) sclerochronology of Callovian (Middle Jurassic) bivalves (*Gryphaea* (*Bilobissa*) *dilobotes*) and belemnites (*Cylindroteuthis puzosiana*) from the Peterborough Member of the Oxford Clay Formation (Cambridgeshire, England): evidence of palaeoclimate, water depth and belemnite behaviour. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **399**: 187–201, doi: https://doi.org/10.1016-/j.palaeo.2014.01.010.

MII H.S., SHI G.R., WANG C.A., 2013 – Late Paleozoic middle-latitude Gondwana environment-stable isotope records from Western Australia. *Gondwana Research*, **24**, 1: 125–138, doi: https://doi.org/10.1016/j.gr.2012.10.013.

NAEF A., 1922 – Die fossilen Tintenfische: eine paläozoologische Monographie. Fischer.

NOSEK B.A., ALTER G., BANKS G.C., BORSBOOM D., BOWMAN S.D., BRECKLER S.J., BUCK S., CHAMBERS C.D., CHIN G., CHRISTENSEN G., CONTESTABILE M., DAFOE A., EICH E., FREESE J., GLENNERSTER R., GOROFF D., GREEN D., HESSE, B., HUMPHREYS M., YARKONI T., 2015 – Promoting an open research culture. *Science*, **348**, 6242: 1422–1425, doi: https://doi.org/10.1126/science.aab2374.

ODUM H.T., 1951 – The stability of the world strontium cycle. *Science*, **114**, 2964: 407–411.

PARIS G., BARTOLINI A., DONNADIEU Y., BEAUMONT V., GAILLARDET J., 2010 – Investigating boron isotopes in a middle Jurassic micritic sequence: Primary vs. diagenetic signal. *Chemical Geology*, **275**, 3/4: 117–126, doi: https://doi.org/10.1016/j.chemgeo.2010.03.013.

PARKINSON D., CURRY G.B., CUSACK M., FALLICK A.E., 2005 – Shell structure, patterns and trends of oxygen and carbon stable isotopes in modern brachiopod shells. *Chemical Geology*, **219**, 1–4: 193–235, doi: https://doi.org/10.1016/j.chemgeo.2005.02.002.

PÉREZ-HUERTA A., CUSACK M., JEFFRIES T.E., WILLIAMS C.T., 2008 – High resolution distribution of magnesium and strontium and the evaluation of Mg/Ca thermometry in Recent brachiopod shells. *Chemical Geology*, **247**, 1/2: 229–241, doi: https://doi.org/10.1016/j.chemgeo.2007.10.014 .

PÉREZ-HUERTA A., CUSACK M., McDONALD S., MARONE F., STAMPANONI M., MACKAY S., 2009 – Brachiopod punctae: a complexity in shell biomineralisation. *Journal of Structural Biology*, **167**, 1: 62–67, doi: https://doi.org/10.1016/j.jsb.2009.03.013.

PIN C., GANNOUN A., DUPONT A., 2014 – Rapid, simultaneous separation of Sr, Pb, and Nd by extraction chromatography prior to isotope ratios determination by TIMS and MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **29**, 10: 1858–1870, doi: https://doi.org/10.1039/C4JA00169A.

PODLAHA O.G., MUTTERLOSE J., VEIZER J., 1998 – Preservation of delta 18 O and delta 13 C in belemnite rostra from the Jurassic/Early Cretaceous successions. *American Journal of Science*, **298**, 4: 324–347.

POGGE von STRANDMANN P., JENKYNS H., WOODFINE R., 2013 – Lithium isotope evidence for enhanced weathering during Oceanic Anoxic Event 2. *Nature Geoscience*, **6**: 668–672, doi: https://doi.org/10.1038/ngeo1875.

POKROY B., FITCH A.N., MARIN F., KAPON M., ADIR N., ZOLOTOYABKO E., 2006 – Anisotropic lattice distortions in biogenic calcite induced by intra-crystalline organic molecules. *Journal of Structural Biology*, **155**, 1: 96–103, doi: https://doi.org/10.1016/j.jsb.2006.03.008.

POPP B.N., PODOSEK F.A., BRANNON J.C., ANDERSON T.F., PIER J., 1986 – ^{87}Sr/^{86}Sr ratios in Permo-Carboniferous sea water from the analyses of well-preserved brachiopod shells. *Geochimica et Cosmochimica Acta*, **50**, 7: 1321–1328, doi: https://doi.org/10.1016/0016-7037(86)90308-X.

POSENATO R., CRIPPA G., de WINTER N.J., FRIJIA G., KASKES P., 2022 – Microstructures and sclerochronology of exquisitely preserved Lower Jurassic lithiotid bivalves: Paleobiological and paleoclimatic significance. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **602**: 111162, doi: https://doi.org/10.1016/j.palaeo.2022.111162.

PRICE G.D., PASSEY B.H., 2013 – Dynamic polar climates in a greenhouse world: Evidence from clumped isotope thermometry of Early Cretaceous belemnites. *Geology*, **41**, 8: 923–926, https://doi.org/10.1130/G34484.1.

PRICE G.D., ROGOV M.A., 2009 – An isotopic appraisal of the Late Jurassic greenhouse phase in the Russian Platform.

Palaeogeography, Palaeoclimatology, Palaeoecology, **273**: 41–49, https://doi.org/10.1016/j.palaeo.2008.11.011.

PRICE G.D., SELLWOOD B.W., 1997 – "Warm" palaeotemperatures from high Late Jurassic palaeolatitudes (Falkland Plateau): Ecological, environmental or diagenetic controls?. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **129**, 3/4: 315–327, doi: https://doi.org/10.1016/S0031-0182(96)00058-2.

PRICE G.D., BAKER S.J., VANDEVELDE J., CLÉMENCE M.-E., 2016 – High-resolution carbon cycle and seawater temperature evolution during the Early Jurassic (Sinemurian-Early Pliensbachian). *Geochemistry, Geophysics, Geosystems*, **17**: 3917–3928, https://doi.org/10.1002/2016GC006541.

PRICE G.D., JANSSEN N.M.M., MARTINEZ M., COMPANY M., VANDEVELDE J.H., GRIMES S.T., 2018 – A high-resolution belemnite geochemical analysis of Early Cretaceous (Valanginian-Hauterivian) environmental and climatic perturbations. *Geochemistry, Geophysics, Geosystems*, **19**: 3832–3843, https://doi.org/10.1029/2018GC007676.

PRICE G.D., HESZLER B., CHARLTON L.M.T., COX J., 2023. A climate perturbation at the Middle–Late Jurassic Transition? Evaluating the isotopic evidence from south-central England. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **628**: 111755, doi: https://doi.org/10.1016/j.palaeo.2023.111755.

REXFORT A., MUTTERLOSE J., 2009 – The role of biogeography and ecology on the isotope signature of cuttlefishes (Cephalopoda, Sepiidae) and the impact on belemnite studies. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **284**, 3/4: 153–163, doi: https://doi.org/10.1016/j.palaeo.2009.09.021.

RIECHELMANN S., MAVROMATIS V., BUHL D., DIETZEL M., EISENHAUER A., IMMENHAUSER A., 2016 – Impact of diagenetic alteration on brachiopod shell magnesium isotope (δ^{26}Mg) signatures: Experimental versus field data. *Chemical Geology*, **440**: 191–206, doi: https://doi.org/10.1016-/j.chemgeo.2016.07.020.

ROLLION-BARD C., SAULNIER S., VIGIER N., SCHUMACHER A., CHAUSSIDON M., LÉCUYER C., 2016 – Variability in magnesium, carbon and oxygen isotope compositions of brachiopod shells: implications for paleoceanographic studies. *Chemical Geology*, **423**: 49–60, doi: https://doi.org/10.1016/j.chemgeo.2019.05.031.

ROMANIN M., CRIPPA G., YE F., BRAND U., BITNER M.A., GASPARD D., HÄUSSERMANN V., LAUDIEN J., 2018 – A sampling strategy for recent and fossil brachiopods: selecting the optimal shell segment for geochemical analyses. *Rivista Italiana di Paleontologia e Stratigrafia*, **124**, 2: 343–359, doi: https://dx.doi.org/10.13130/2039-4942/10193.

ROSALES I., QUESADA S., ROBLES S., 2004 – Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque-Cantabrian basin, northern Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **203**: 253–275, https://doi.org/10.1016/S0031-0182(03)00686-2.

ROSENTHAL Y., FIELD M.P., SHERRELL R.M., 1999 – Precise determination of element/calcium ratios in calcareous samples using sector field inductively coupled plasma mass spectrometry. *Analytical chemistry*, **71**, 15: 3248–3253, doi: https://doi.org/10.1021/ac981410x.

SAVARD M.M., VEIZER J., HINTON R., 1995 – Cathodoluminescene at low Fe and Mn concentrations; a SIMS study of zones in natural calcites. *Journal of Sedimentary Research*, **65**, 208–213.

SCHELL B.R., BRUNS N., 2024 – Lab sustainability programs LEAF and My Green Lab®: impact, user experience & suitability. *RSC Sustainability*. doi: https://doi.org/10.1039/d4su00387j.

SCHÖNE B.R., 2013 – *Arctica islandica* (Bivalvia): a unique paleoenvironmental archive of the northern North Atlantic Ocean. *Global and Planetary Change*, **111**: 199–225, doi: https://doi.org/10.1016/j.gloplacha.2013.09.013.

SCHÖNE B., OSCHMANN W., TANABE K., DETTMAN D., FIEBIG J., HOUK S.D., KANIE Y., 2004 – Holocene seasonal environmental trends at Tokyo Bay, Japan, reconstructed from bivalve mollusk shells – implications for changes in the East Asian monsoon and latitudinal shifts of the Polar Front. *Quaternary Science Reviews*, **23**, 9/10: 1137–1150, doi: https://doi.org/10.1016/j.quascirev.2003.10.013.

SCHÖNE B.R., ZHANG Z., RADERMACHER P., THÉBAULT J., JACOB D.E., NUNN E.V., MAURER A.F., 2011 – Sr/Ca and Mg/Ca ratios of ontogenetically old, long-lived bivalve shells (Arctica islandica) and their function as paleotemperature proxies. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **302**, 1/2: 52–64, doi: https://doi.org/10.1016/j.palaeo.2010.03.016.

SCHRAG D.P., 1999 – Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. *Paleoceanography*, **14**, 2: 97–102, doi: https://doi.org/10.1029/1998PA900025.

SØRENSEN A.M., ULLMANN C.V., THIBAULT N., KORTE C., 2015 – Geochemical signatures of the early Campanian belemnite *Belemnellocamax mammillatus* from the Kristianstad Basin in Scania, Sweden. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **433**: 191–200, doi: https://doi.org/10.1016/j.palaeo.2015.05.025.

SPÖTL C., VENNEMANN T.W., 2003 – Continuous-flow isotope ratio mass spectrometric analysis of carbonate minerals. *Rapid Communications in Mass Spectrometry*, **17**, 9: 1004–1006, doi: https://doi.org/10.1002/rcm.1010.

STANLEY S.M., HARDIE L.A., 1998 – Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **144**, 1/2: 3–19, doi: https://doi.org/10.1016/S0031-0182(98)00109-6.

STEUBER T., 1996 – Stable isotope sclerochronology of rudist bivalves: growth rates and Late Cretaceous seasonality. *Geology*, **24**, 4: 315–318, doi: https://doi.org/10.1130/0091-7613-(1996)024<0315:SISORB>2.3.CO;2.

STEUBER T., VEIZER J., 2002 – Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. *Geology*, **30**, 12: 1123–1126, doi: https://doi.org/10.1130/0091-7613(2002)030<1123:PROPTC>2.0.CO;2.

STEVENS K., GRIESSHABER E., SCHMAHL W., CASELLA L.A., IBA Y., MUTTERLOSE J., 2017 – Belemnite biomineralization, development, and geochemistry: The complex rostrum of *Neohibolites minimus*. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **468**: 388–402, doi: https://doi.org/10.1016/j.palaeo.2016.12.022.

STICHLER W., 1995 – Interlaboratory comparison of new materials for carbon and oxygen isotope ratio measurements. In Reference and intercomparison materials for stable isotopes of light elements (Vol. 825, pp. 67–74). IAEA TECDOC-825, International Atomic Agency Vienna, Austria.

SUAN G., MATTIOLI E., PITTET B., LÉCUYER C., SUCHÉRAS-MARX B., DUARTE L.V., PHILIPPE M., REGGIANI L., MARTINEAU F., 2010 – Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters*, **290**, 3/4: 448–458, doi: https://doi.org/10.1016/j.epsl.2009.12.047.

SWART P.K., 2015 – The geochemistry of carbonate diagenesis: The past, present and future. *Sedimentology*, **62**, 5: 1233–1304, https://doi.org/10.1111/sed.12205.

TAKAYANAGI H., ASAMI R., OTAKE T., ABE O., MIYAJIMA T., KITAGAWA H., IRYU Y., 2015 – Quantitative analysis of intraspecific variations in the carbon and oxygen isotope compositions of the modern cool-temperate brachiopod *Terebratulina crossei*. *Geochimica et Cosmochimica Acta*, **170**: 301–320, doi: https://doi.org/10.1016/j.gca.2015.08.006.

ULLMANN C.V., KORTE C., 2015 – Diagenetic alteration in low-Mg calcite from macrofossils: a review. *Geological Quarterly*, **59**, 1: 3–20, doi: https://doi.org/10.7306/gq.1217.

ULLMANN C.V., POGGE von STRANDMANN P.A., 2017 – The effect of shell secretion rate on Mg/Ca and Sr/Ca ratios in biogenic calcite as observed in a belemnite rostrum. *Biogeosciences*, **14**, 1: 89–97, https://doi.org/10.5194/bg-14-89-2017.

ULLMANN C.V., CAMPBELL H.J., FREI R., HESSELBO S.P., POGGE von STRANDMANN P.A.E., KORTE C., 2013a – Partial diagenetic overprint of Late Jurassic belemnites from New Zealand: Implications for the preservation potential of δ^7Li values in calcite fossils. *Geochimica et Cosmochimica Acta*, **120**: 80–96, doi: https://doi.org/10.1016/j.gca.2013.06.029.

ULLMANN C.V., HESSELBO S.P., KORTE C., 2013b – Tectonic forcing of Early to Middle Jurassic seawater Sr/Ca. *Geology*, **41**, 12: 1211–1214, doi: https://doi.org/10.1130/G34817.1.

ULLMANN C.V., THIBAULT N., RUHL M., HESSELBO S.P., KORTE C., 2014 – Effect of a Jurassic oceanic anoxic event on belemnite ecology and evolution. *Proceedings of the National Academy of Sciences*, **111**, 28: 10073–10076, doi: https://doi.org/10.1073/pnas.132015611.

ULLMANN C.V., FREI R., KORTE C., HESSELBO S.P., 2015 – Chemical and isotopic architecture of the belemnite rostrum. *Geochimica et Cosmochimica Acta*, **159**: 231–243, doi: https://doi.org/10.1016/j.gca.2015.03.034.

ULLMANN C.V., FREI R., KORTE C., LÜTER C., 2017a – Element/Ca, C and O isotope ratios in modern brachiopods: Species-specific signals of biomineralization. *Chemical Geology*, **460**: 15–24, doi: https://doi.org/10.1016/j.chemgeo.2017.03.034.

ULLMANN C.V., KORTE C., BITNER M.A., AZMY K., BRAND U., 2017b – Geochemistry of the brachiopod *Hemithiris psittacea* from the Canadian Arctic: implications for high latitude palaeoclimate studies. *Chemical Geology*, **466**: 187–198, doi: https://doi.org/10.1016/j.chemgeo.2017.06.007.

ULLMANN C.V., GALE A.S., HUGGETT J., WRAY D., FREI R., KORTE C., BROOM-FENDLEY S., LITTLER K., HESSELBO S.P., 2018 – The geochemistry of modern calcareous barnacle shells and applications for palaeoenvironmental studies. *Geochimica et Cosmochimica Acta*, **243**: 149–168, doi: https://doi.org/10.1016/j.gca.2018.09.010.

ULLMANN C.V., BOYLE R., DUARTE L.V., HESSELBO S.P., KASEMANN S.A., KLEIN T., LENTON T.M., PIAZZA V., ABERHAN M., 2020 – Warm afterglow from the Toarcian Oceanic Anoxic Event drives the success of deep-adapted brachiopods. *Scientific Reports*, **10**, 1: 6549, doi: https://doi.org/10.1038/s41598-020-63487-6.

UREY H.C., 1947 – The thermodynamic properties of isotopic substances. *Journal of the Chemical Society* (Resumed), 562–581.

UREY H.C., 1948 – Oxygen isotopes in nature and in the laboratory. *Science*, **108**, 2810: 489–496.

UREY H.C., LOWENSTAM H.A., EPSTEIN S., McKINNEY R.C., 1951 – Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and the southeastern United States. *Bulletin of the Geological Society of America*, **62**, 399–416.

VEIZER J., 1974 – Chemical diagenesis of belemnite shells and possible consequences for paleotemperature determinations. *Neues Jahrbuch fü Geologie und Paläontologie, Abhandlungen*, **147**: 91–111.

VEIZER J., 1983 – Chemical diagenesis of carbonates: Theory and trace element technique. *In*: Stable Isotopes in sedimentary geology, *SEPM*, short course No. **10**; (Eds. M.A. Arthur *et al.*). Society of Economic Paleontologists and Mineralogists: Tulsa, OK, USA, 1983; 3-1–3-100.

VEIZER J., BRUCKSCHEN P., PAWELLEK F., DIENER A., PODLAHA O.G., CARDEN G.A., JASPER T., KORTE C., STRAUSS H., AZMY K., ALA D., 1997 – Oxygen isotope evolution of Phanerozoic seawater. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **132**: 1–4: 159–172, doi: https://doi.org/10.1016/S0031-0182(97)00052-7.

VEIZER J., ALA D., AZMY K., BRUCKSCHEN P., BUHL D., BRUHN F., CARDEN G.A., DIENER A., EBNETH S., GODDERIS Y., JASPER T., KORTE C., PAWELLEK F., PODLAHA O.G., STRAUSS H., 1999 – ^{87}Sr/^{86}Sr, δ^{13}C and δ^{18}O evolution of Phanerozoic seawater. *Chemical Geology*, **161**, 1–3: 59–88, doi: https://doi.org/10.1016/S0009-2541(99)00081-9.

VETTER L., SPERO H.J., RUSSELL A.D., FEHRENBACHER J.S., 2013 – LA-ICP-MS depth profiling perspective on cleaning protocols for elemental analyses in planktic foraminifers. *Geochemistry, Geophysics, Geosystems*, **14**, 8: 2916–2931, doi: https://doi.org/10.1002/ggge.20163.

VICKERS M.L., FERNANDEZ A., HESSELBO S.P., PRICE G.D., BERNASCONI S.M., LODE S., ULLMANN C.V., THIBAULT N., HOUGAARD I.W., KORTE C., 2020 – Unravelling Middle to Late Jurassic palaeoceanographic and palaeoclimatic signals in the Hebrides Basin using belemnite clumped isotope thermometry. *Earth and Planetary Science Letters*, **546**: 116401, doi: https://doi.org/10.1016/j.epsl.2020.116401.

VOIGT S., WILMSEN M., MORTIMORE R.N., VOIGT T., 2003 – Cenomanian palaeotemperatures derived from the oxygen isotopic composition of brachiopods and belemnites: evaluation of Cretaceous palaeotemperature proxies. *International Journal of Earth Sciences*, **92**: 285–299, doi: https://doi.org/10.1007/s00531-003-0315-1.

WASHINGTON K.E., WEST A.J., KALDERON-ASAEL B., KATCHINOFF J.A., STEVENSON E.I., PLANAVSKY N.J., 2020 – Lithium isotope composition of modern and fossilized Cenozoic brachiopods. *Geology*, **48**, 11: 1058–1061, doi: https://doi.org/10.1130/G47558.1.

WEFER G., BERGER W.H., 1991 – Isotope paleontology: growth and composition of extant calcareous species. *Marine Geology*, **100**, 1–4: 207–248, https://doi.org/10.1016/0025-3227(91)90234-U.

WESTERHOLD T., MARWAN N., DRURY A.J., LIEBRAND D., AGNINI C., ANAGNOSTOU E., BARNET J.S., BOHATY S.M., DE VLEESCHOUWER D., FLORINDO F., FREDERICHS T., HODELL D.A., HOLBOURN A.E., KROON D., LAURETANO V., LITTLER K., LOURENS L.J., LYLE M., PÄLIKE H., RÖHL U., TIAN J., WILKENS R.H., WILSON P.A., ZACHOS J.C., 2020 – An astronomically dated record of Earth's climate and its predictability over the last 66 million years. *Science*, **369**, 6509: 1383–1387, doi: https://doi.org/10.1126/science.aba6853.

WIERZBOWSKI H., 2013 – Life span and growth rate of Middle Jurassic mesohibolitid belemnites deduced from rostrum microincrements. *Volumina Jurassica*, **11**, 1: 1–18.

WIERZBOWSKI H., 2015 – Seawater temperatures and carbon isotope variations in central European basins at the Middle–Late Jurassic transition (Late Callovian–Early Kimmeridgian). *Palaeogeography, Palaeoclimatology, Palaeoecology*, **440**: 506–523, doi: https://doi.org/10.1016/j.palaeo.2015.09.020.

WIERZBOWSKI H., 2021 – Advances and challenges in palaeoenvironmental studies based on oxygen isotope composition of skeletal carbonates and phosphates. *Geosciences*, **11**, 10: 419.

WIERZBOWSKI H., JOACHIMSKI M., 2007 – Reconstruction of late Bajocian–Bathonian marine palaeoenvironments using carbon and oxygen isotope ratios of calcareous fossils from the Polish Jura Chain (central Poland). *Palaeogeography, Palaeoclimatology, Palaeoecology*, **254**, 3/4: 523–540.

WIERZBOWSKI H., JOACHIMSKI M.M., 2009 – Stable isotopes, elemental distribution, and growth rings of belemnopsid belemnite rostra: proxies for belemnite life habitat. *Palaios*, **24**, 6: 377–386, https://doi.org/10.2110/palo.2008.p08-101r.

YARRA T., BLAXTER M., CLARK M.S., 2021 – A bivalve biomineralization toolbox. *Molecular Biology and Evolution*, **38**, 9: 4043–4055, doi: https://doi.org/10.1093/molbev/msab153.

YE F., CRIPPA G., ANGIOLINI L., BRAND U., CAPITANI G., CUSACK M., GARBELLI C., GRIESSHABER E., HARPER E., SCHMAHL W., 2018 – Mapping of recent brachiopod microstructure: a tool for environmental studies. *Journal of Structural Biology*, **201**, 3: 221–236, doi: https://doi.org/10.1016/j.jsb.2017.11.011.

ZACHOS J., PAGANI M., SLOAN L., THOMAS E., BILLUPS K., 2001 – Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science*, **292**: 686–693.

ZOLOTOYABKO E., CASPI E.N., FIERAMOSCA J.S., VON DREELE R.B., MARIN F., MOR G., ADDADI L., WEINER S., POLITI Y., 2010 – Differences between bond lengths in biogenic and geological calcite. *Crystal Growth & Design*, **10**, 3: 1207–1214, doi: https://doi.org/10.1021/cg901195t.